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An Introduction to Polymer Physics

Mir Publishers Moscow



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ВВЕДЕНИЕ В ФИЗИКУ ПОЛИМЕРОВ

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An Introduction to Polymer Physics

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Preface

The vigorous development of polymer science and the extensive utilization of polymeric materials in technology has led in recent years to the increased interest to the various problems of the physics of polymers. Polymer physics is highly important for the understanding of many scientific and practical problems associated with the use of polymeric materials in modern engineering. This accounts for the fact that not only physicists but also synthetical chemists, technologists and structural engineers become more and more interested in numerous problems of the physics of polymers. At present there are practically no monographs in the USSR that could offer a concise survey of the basic concepts and ideas of the modern physics of polymers.

Attempts have repeatedly been made (1-8) to write monographs devoted to polymer physics. The four-volume book by H. A. Stuart published in 1956 is in fact a collection of articles written by various authors. The problems discussed by the authors are uncorrelated and the articles are written in different languages. The book by Stuart was the first and rather unsuccessful attempt to write a book devoted to the general problems of polymer physics. The two-volume book *Macromolecular Physics* by B. Wunderlich (2) is mainly concerned with the problems of the structure and crystallization of polymers. A number of monographs have been published at various times (they have long been out of print) which are concerned with important but specialized problems of polymer physics. Mention should be made of the excellently written monograph by M. V. Vol'kenshtein *Configurational Statistics of Polymeric Chains* (3) and the books by Alfrey (4), Treloar (5) and Ward (6) which deal with the mechanical properties of polymers. However, books that would offer, in a compact and available form, an exposition of the fundamentals of modern physics of polymers have not yet appeared. In 1976 an attempt was made to bridge this gap—the book by G. M. Bartenev and Yu. V. Zelenev was published (7), which, as the authors emphasized in the preface, is “an introduction to the physics of the condensed state of mostly noncrystallizable polymers”. The monograph written by Bartenev and Zelenev is in fact devoted to the physics of elastomers. But polymers that have found wide practical application are those in the glassy state (linear and cross-linked polymers) and also crystalline polymers.

The modern physics of polymers is a rather peculiar combination of the basic concepts, ideas and methods of molecular physics, thermodynamics, statistical physics and solid-state physics. It is this complex combination of sciences that accounts for the difficulties that arise when attempts are made to write monographs on the physics of polymers.

The purpose of this monograph is to present a systematic exposition of the basic conceptions of modern polymer physics in a sufficiently rigorous form which will nevertheless be understandable even to the non-specialist. It is hoped that the acquaintance with this monograph will allow the reader to quickly cover the entire range of basic ideas and problems of the present-day physics of polymers and subsequently to take up a more detailed scrutiny of specialized problems.

It is known that one of the main objectives of polymer physics is the elucidation of the relationship between the chemical and physical structure and the

physical properties of polymers. This is what dictated the choice of the material expounded in this book. Apart from the questions, which are traditional in the literature concerned with the physical and physico-chemical properties of polymers (the chemical and physical structure, the physical states, strength), this book also deals with less traditional problems (the thermal and dielectric properties of polymers, the nuclear magnetic resonance of polymers).

A distinctive feature of this book is the consideration of important problems of the physics of polymers (Chapters 4-6) in the light of the ideas of modern solid-state physics. The author believes that such an approach, while not detracting from the polymeric specificity of the book, allows the use of the concepts and methods of solid-state physics.

This monograph presents a brief survey of the theory of the main physical properties of polymers. An attempt has been made to show their interrelationships and to outline the principal problems that arise in their study.

References

1. Stuart, H. A., *Die Physik der Hochpolymeren*, volumes 1-4, Berlin, Springer Verlag, 1952-1956.
2. Wunderlich, B., *Macromolecular Physics*, Academic Press, New York, 1973.
3. Volkenstein, M. B., *Configurational Statistics of Polymeric Chains*, Interscience, New York, 1963.
4. Alfrey, T., *Mechanical Behaviour of High Polymers*, Interscience, New York, 1948.
5. Treloar, L. R. G., *Physics of Rubber Elasticity*, Oxford University Press, Oxford, 1958.
6. Ward, I. M., *Mechanical Properties of Solid Polymers*, Wiley-Interscience, London, 1971.
7. Bartenev, G. M. and Yu. V. Zelenev, *A Course of Polymer Physics*, Khimiya, Leningrad, 1976 (in Russian).
8. Holzmüller, W. and K. Altenburg, *Physik der Kunststoffe*, Akademie Verlag, Berlin, 1961.

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Chapter 1

Introduction to Macromolecular Physics

1.1. The Chemical Structure of Polymers

The most important physical properties of polymers are determined by their chemical structure. At first glance it may seem that many of the properties, especially the properties of crystalline polymers, are governed mainly by their structure. In actual fact, however, this or that type of the supermolecular organization (in all its variety) depends in the final run on the chemical structure of the polymeric chain. A polymeric chain conveys important information on the possible supermolecular organization of the polymer, its main physical properties and also on optimal processing conditions. This information is probably specified during polymer synthesis by the nature of the mutual arrangement of atoms, atomic groups, repeating units, and also by the molecular mass and, evidently, by the molecular-mass distribution. Unfortunately, we have not yet discovered the code that could be used, with the chemical structure of the polymeric chain being known, to decipher the information contained in it. The main task in the physics of polymers is precisely to find this code. Thus, the principal problem in polymer physics—the establishment of the relationship between the chemical and physical structure and the physical properties of polymers—is in fact analogous to the problem of the Rosetta Stone with the aid of which Jean Francois Champollion found the key to the deciphering of the ancient Egyptian hieroglyphics.

Let us consider some features of the chemical structure that determine the most important and most specific properties of polymers.

Polymers are compounds whose molecules are sequences of a large number of recurring identical atomic groupings joined through chemical bonds. The recurring atomic groupings that make up a polymeric chain have come to be known as repeating or repeat units (or monomeric units). It should be noted that very frequently the repeating unit differs substantially from the monomer, the polymerization of which leads to the formation of a polymer.

Thus, a macromolecule or a polymeric chain is built up of a large number of repeating units. One of the most significant parameters of polymers is their molecular mass M , which is determined by the number p of repeating units that make up the macromolecule:

$$M = pM_0 \quad (1.1)$$

where M_0 is the molecular mass of the repeating unit.

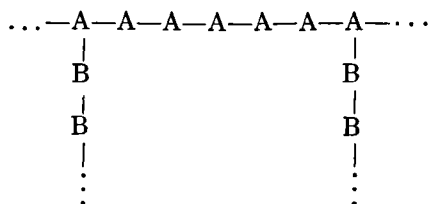
The parameter p is called the degree of polymerization. If the value of p is not large, then a substance consisting of such molecules is an oligomer. For instance, at $p = 2$ we have a dimer, and at $p = 3$, a trimer, etc. The degree of polymerization may amount to 10^4 . In this case the molecular mass of such a high polymer may reach 10^6 .

A specific feature of synthetic polymers is that the molecular masses of individual chains may differ considerably from the average molecular mass of the polymer. A real polymer is a mixture of macromolecules with different molecular masses. That is why every polymer is characterized by its own molecular-mass distribution. This salient feature of synthetic polymers renders them different from biopolymers, which have, as a rule, a strictly definite molecular mass.

Polymers may exist as linear, branched and cross-linked chain structures.

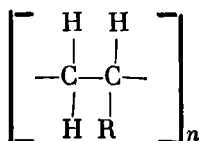
Linear polymers have long chains composed of a large number of repeating units. If we label the repeating unit by the letter A, the chemical formula of a linear polymer can be depicted as $\dots - A - A - A - A - \dots$. Typical representatives of linear polymers are polyethylene, polytetrafluoroethylene, and polycapramide.

Branched polymers have side chains attached to their main chain. If the side chains consist of identical repeating units, which we shall label by the letter B, then the chemical formula of a branched polymer may be written thus:



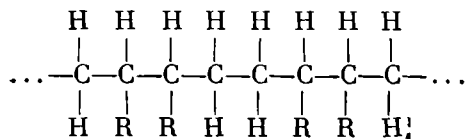
As an example of branched polymers may be cited polymethyl methacrylate.

Cross-linked polymers have a three-dimensional space network formed by means of chemical bonds. According to the order in which the repeating units are arranged in the chain, polymers are classified into regular and irregular (random) structures. Random disposition of repeating units in a polymer chain may arise from the various ways by which the monomeric units are linked upon polymerization. For example, in polymers of the vinyl series which have the chemical formula

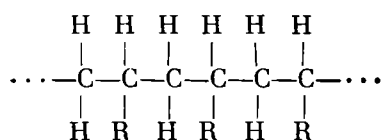


(where R may be a chlorine or fluorine atom, or a phenyl group, etc.), the repeating units can be joined in two ways: (1) in a head-to-head (head-to-head-tail-to-tail) manner; and (2) in a head-to-tail manner.

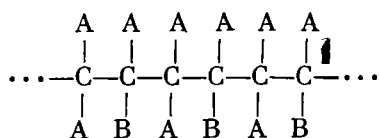
In the first case the chain will have the following appearance:



In the second case the repeating units in the polymer chain are arranged in a different fashion:

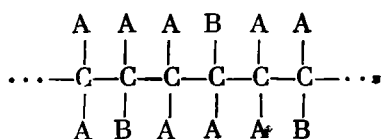


The head-to-tail linkage of repeating units is most frequently realized during synthesis. If the repeating units are arranged in the polymer chain in a head-to-head or tail-to-tail manner, the polymer is said to be irregular. In this latter case the polymer is referred to as an atactic polymer. Of importance are stereoregular polymers in which all the repeating units and all the side chains are arranged in a strictly definite order. Stereoregularity is most prominently displayed in isotactic and syndiotactic polymers. Isotactic polymers are those in which the repeating units have the same configuration. The chemical structure of an isotactic polymer can be depicted as follows:



(where A and B are certain radicals, and $A \neq B$).

In syndiotactic polymers the adjacent repeating units have opposite spatial configurations. The chemical structure of a syndiotactic polymer may be depicted thus:]



The physical properties of isotactic or syndiotactic polymers differ significantly from the corresponding properties of atactic polymers. For instance, atactic polystyrene is an amorphous polymer which cannot be crystallized. Isotactic polystyrene is a partly crys-

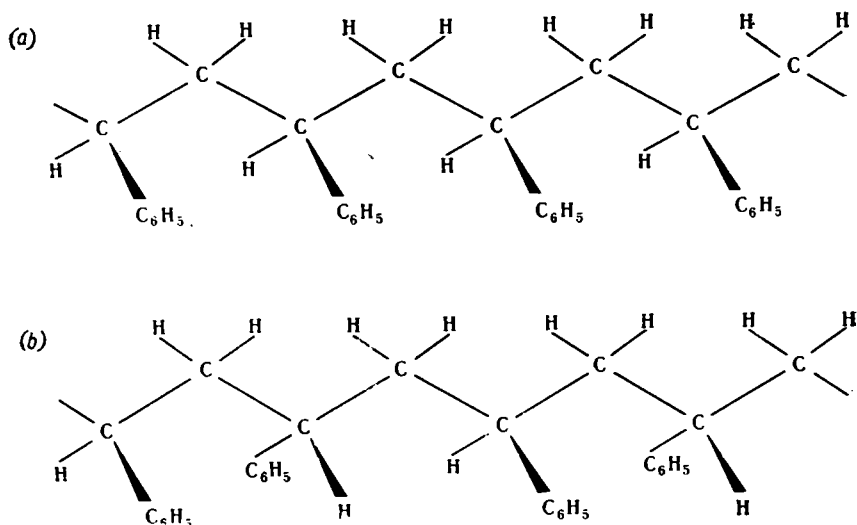
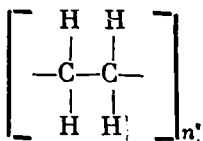


Fig. 1.1. The chains of isotactic (a) and syndiotactic (b) polystyrene.

talline polymer. Atactic polyvinyl chloride is practically an amorphous polymer (its degree of crystallinity is 10-15 per cent). Syndiotactic polyvinyl chloride is a highly crystalline polymer (the experimental degree of crystallinity of this polymer is 90 per cent). Stereoregularity can most often be produced in polymers with an asymmetric potential barrier (for example, in polymers of the vinyl series). An example of such polymers is polystyrene. Figure 1.1 shows the arrangement of repeating units and phenyl groups (the role of the radical B is played by the group C_6H_5) in the chains of isotactic and syndiotactic polystyrene.

We shall now consider the chemical structure of some frequently encountered polymers and trace out the manner in which it affects their properties.

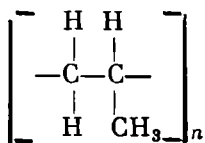
1. Polyethylene has the simplest chemical structure:



This is one of the most often used polymers. It exhibits the ability to undergo, even at room temperature, large reversible (or recoverable) deformations. The density of this polymer may vary from 0.852 g/cm^3 (a completely amorphous sample) to 1 g/cm^3 (a fully crystalline sample). At the same time, the strength of this polymer is not high. The melting temperature of polyethylene (depending on the type of polymer) ranges from 110 to 140°C . The glass-transition

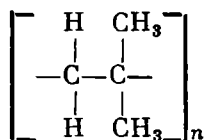
temperature of completely amorphous polyethylene is evidently equal to -80°C .

2. Polypropylene which has the structure



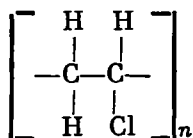
differs from polyethylene in that in its repeating unit one hydrogen atom is replaced by a methyl group. Incidentally, the properties of this polymer differ from the properties of polyethylene. It is stronger, has a higher glass-transition temperature (-20°C) and a higher melting point (176°C).

3. Polyisobutylene with the chemical structure



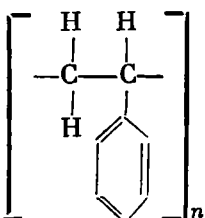
differs in its chemical structure from polypropylene: its repeating unit contains two CH_3 groups instead of one. As regards physical properties, however, this is a quite different polymer as compared with polypropylene. For example, at room temperature it is in the rubbery (high-elastic) state and readily changes its shape even under the influence of its own weight.

4. Polyvinyl chloride which has the following chemical structure



is a typical polymer of the vinyl series. It is different from polyethylene in that its repeating unit contains a chlorine atom in place of one of the hydrogen atoms. Even such a slight difference leads to the formation of a completely new polymer, which is stronger and has a considerably higher glass-transition temperature (80°C).

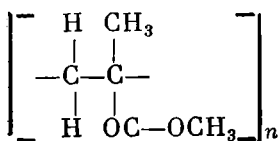
5. Polystyrene



is also a polymer of the vinyl series and differs from polyvinyl chloride only by the type of substituent. The substituent in the repeating

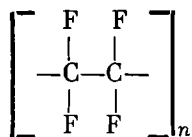
unit of polystyrene is the phenyl group, C_6H_5 , instead of the chlorine atom. Polystyrene is a transparent, strong, and somewhat brittle amorphous polymer, whose glass-transition temperature is $100^\circ C$. Isotactic polystyrene is able to crystallize.

6. Polymethyl methacrylate



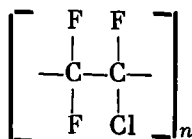
is known under the name of Plexiglas or organic glass. This is a transparent, highly strong, amorphous polymer.

7. Polytetrafluoroethylene (known as Teflon)



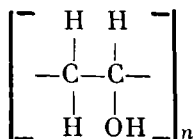
has a density (high for a polymer) ranging from 2.0 g/cm^3 (a completely amorphous sample) to 2.3 g/cm^3 (a completely crystalline sample). It is marked for its extremely high chemical stability, a high melting point ($327^\circ C$) and a low glass-transition temperature ($-100^\circ C$). Even at room temperature polytetrafluoroethylene displays cold flow: it can easily be deformed even under the influence of a small load. Such a behaviour is typical of some low-molecular-mass substances, so-called plastic crystals, whose distinctive feature is internal rotation. The internal rotation of the units of the polymeric chain is the specific feature of polytetrafluoroethylene. Polytetrafluoroethylene is an excellent dielectric. The dielectric loss tangent for this polymer is about 10^{-5} .

8. Polytrifluorochloroethylene



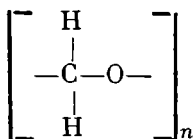
differs from polytetrafluoroethylene in that one of the fluorine atoms in its repeating unit is replaced by a chlorine atom. Such substitution leads to a sharp decrease in the melting point ($T_m = 220^\circ C$), an increase in the dielectric loss tangent (dissipation factor), and to an increase in its mechanical strength. The degree of crystallinity of this polymer may vary from 0 to 80 per cent.

9. Polyvinyl alcohol



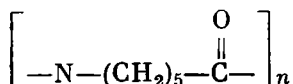
is a crystalline polymer, which is used for the manufacture of fibres and films. It is exactly from polyvinyl alcohol that the physicists and technologists from Leningrad produced a few years ago the champion fibre which has a very high strength.

10. Polyformaldehyde (polyoxymethylene)



is a polyether and a representative of heterochain polymers. This is a highly crystalline, strong polymer, which is finding an ever increasing application. Miniature single crystals of polyformaldehyde were produced several years ago by the radiation-induced solid-phase polymerization of trioxane.

11. Polycapramide (Nylon 6)



is a member of the class of polyamides. This crystalline polymer (the degree of crystallinity 50-60 per cent), which is very strong, is widely employed for the production of fibres and films.

From the examples given above it is seen that even a slight change in the chemical formula of the repeating unit results in a substantial change in the physical properties of polymers. It might seem that such a difference in physical properties between various polymers would not allow the description of these properties from the standpoint of a single physical theory. However, in actual fact the situation is not so hopeless as might seem at first sight. There are at least two regions in which the physical properties of polymers can be described from a unified viewpoint within the framework of a single physical theory.

First, at low temperatures one can describe the physical properties of both crystalline and amorphous polymers in the glassy state by using the ideas and conceptions of modern solid-state physics. Second, the behaviour of polymers in the rubbery (high-elastic) state can be depicted within the framework of the conceptions of statistical physics and thermodynamics. Chronologically, the statistical physics of polymers in the rubbery state had been developed

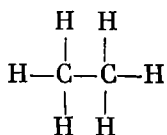
earlier, and it made it possible to account for the most important and specific feature of polymers—the ability to undergo large recoverable deformations. This was possible because polymers having different chemical structures were found to have a common feature—in the rubbery state all polymers exhibit internal rotation. It should be remarked that the use of the basic concepts and mathematical apparatus of statistical physics for the description of the behaviour of polymers in the rubbery state is possible due primarily to the fact that polymeric molecules consist of a very large number of identical repeating units and an even larger number of atoms.

1.2. Internal Rotation. Configurations and Conformations of Macromolecules

When polymer science was originally developed, scientists imagined macromolecules as rigid rods. On the basis of this model it was impossible to account for the ability of polymers to experience large recoverable deformations. In this connection, there was developed a concept according to which macromolecules have the form of helices, which can be extended under the influence of mechanical stress. It was, however, found later that many polymers are not helices at all. For example, the chains of a number of polymers have a planar zig-zag shape.

It has been established that the ability of many polymers to undergo large recoverable deformations is associated with the internal rotation of the individual parts of macromolecules relative to one another. The internal rotation has been studied rather extensively in the case of low-molecular-mass organic compounds. It was originally presumed that the internal rotation occurred without change of the energy of the molecule. Such rotation is called free internal rotation. At a later time S. E. Bresler and Ya. I. Frenkel showed that the internal rotation in macromolecules is not free because of the interaction between atoms that are not joined through chemical bonds.

Let us examine the internal rotation in the simplest form, taking the ethane molecule as an example. Ethane has the following chemical structure:



In the ethane molecule (see Fig. 4.2) the rotation of one methyl group relative to the other occurs about the C—C bond. One can imagine two most specific positions of one CH₃ group relative to the other (see Fig. 1.3). The first position in which the distance between the hydrogen atoms is minimal is the least stable since the repulsive

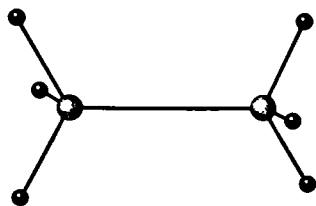
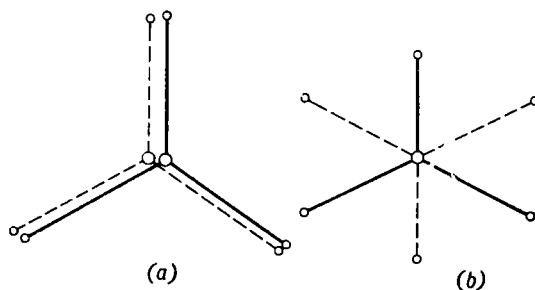


Fig. 1.2. The model of the ethane molecule.

Fig. 1.3. The arrangement of the CH_3 groups in the ethane molecule in the *cis*-position (a) and in the *trans*-position (b).

forces that operate between the hydrogen atoms will tend to rotate the CH_3 group. It is obvious that in this position the methyl group has a maximum of the potential energy. Upon rotation by 60° , while being in the staggered position (the *trans*-position) the CH_3 group of ethane will have a minimum of the potential energy. Obviously, when the angle of rotation is changed, the potential energy of the methyl group is also altered (see Fig. 1.4).

In order to make the CH_3 group flip from the position corresponding to one minimum of potential energy to the position corresponding to the adjacent minimum, it must have a kinetic energy exceeding the height of the potential barrier U_0 (or equal to this value). For ethane and a number of other molecules, in which the rotation about the C_3 symmetry axis is possible, the potential energy of internal rotation depends on the angle of rotation φ in accordance with the following approximate formula:

$$U = \frac{U_0}{2} (1 - \cos 3\varphi) \quad (1.2)$$

The height of the potential barrier U_0 which restricts the rotation of the kinetic elements of molecules is determined by the magnitude of the energy of intra- or intermolecular interaction. For the ethane molecule $U_0 = 12.1$ kJ/mole. Below are given the potential barriers heights (in kJ/mole) for a number of organic compounds:

Compound	U_0	Compound	U_0
$\text{H}_3\text{C}-\text{CH}_3$	12.1	$\text{H}_3\text{C}-\text{CH}_2\text{F}$	13.9
$\text{H}_3\text{C}-\text{C}_2\text{H}_5$	14.2	$\text{H}_3\text{C}-\text{CH}_2\text{Cl}$	15.5
$\text{H}_3\text{C}-\text{CH}(\text{CH}_3)_2$	16.3	$\text{H}_3\text{C}-\text{OH}$	4.5
$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_3$	18.4	$\text{H}_3\text{Si}-\text{SiH}_3$	4.2

From the data given above we can see that the value of U_0 increases upon replacement of the hydrogen atoms in the ethane molecule by halogen atoms (F, Cl) and diminishes if the rotation takes place about the C—O or Si—Si bonds.

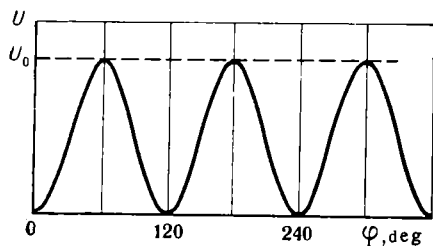


Fig. 1.4. The potential energy of the ethane molecule versus the angle of rotation of the CH_3 group.

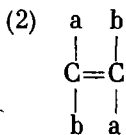
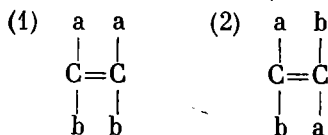
If the energy of thermal motion of some atomic group in the molecule is lower than the potential barrier height, this group cannot leave the position corresponding to the minimum of the potential energy and it performs vibrations about the position with a minimum of the potential energy. This type of thermal motion is called *hindered* (or *retarded*) rotation.

Molecules that have a more complex chemical structure than the ethane molecule usually have several minima of the potential energy; the energy values corresponding to these minima may vary. The result is that to different conformations of the polymer chain there correspond different energies.

The *conformation* is such an arrangement of atoms or atomic groups in a molecule which can be changed by the rotation of the individual portions of the molecule without the destruction of chemical bonds. Figure 1.3 shows two possible conformations of the ethane molecule.

In contrast to the conformation, the *configuration* refers to the arrangement in space of atoms in the molecule which cannot be changed by the rotation of individual parts of the molecule without destroying and reforming chemical bonds.

For example, molecules containing a double bond and two different substituents, a and b, adopt the following configurations:



In the first case we have a *cis*-isomer and in the second, a *trans*-isomer. The transition from one of these configurations to the other is impossible without rupture of the chemical bonds, since the rotation about the double bonds is impossible. Typical examples of such *cis*- and *trans*-isomers are maleic and fumaric acids.

In a polymeric chain consisting of single C—C bonds the internal rotation is possible in each unit. In such a case the chain can adopt various conformations. It is the internal rotation that determines the flexibility of the polymeric chain, which in its turn is responsible for large recoverable deformations, which constitute a special feature of polymers.

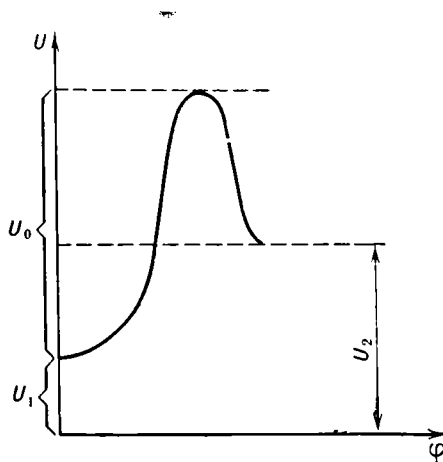


Fig. 1.5. The potential energy of a polymeric chain versus the angle of rotation of the repeating unit.

1.3. The Flexibility of Macromolecules

It is obvious that the potential energy $U(\varphi)$ of a polymer chain (φ is the angle of rotation) will be changed upon rotation of the individual links of the chain about one another. In this case the dependence $U(\varphi)$ may be represented by a curve with several minima of the potential energy. Let the position of the repeating unit of the molecule at some moment of time be determined by the potential energy U_1 , and the position that will be occupied by this unit as the result of thermal motion after a certain interval of time be characterized by the potential energy U_2 (Fig. 1.5). The quantity $\Delta U = U_2 - U_1$, equal to the energy difference between these two positions, is a measure of the *thermodynamic flexibility* of the chain, which determines the ability of the chain to alter its conformation. The lower the value of ΔU the higher is the probability of conformational transitions of the polymeric chain. As a result of thermal motion, a sufficiently long macromolecule having high flexibility (a low value of ΔU) coils, forming a *random-coil configuration*. It will be shown at a later time that the thermodynamic flexibility characterizes the amount of coiling of the random coil. However, while characterizing the possibility of conformational transitions, the thermodynamic flexibility does not allow us to estimate their rates. The rate of the flip from one conformation to another depends on the relation between the energy of the unit and the potential barrier height U_0 that must be surmounted by that unit. The quantity U_0 is called the *kinetic flexibility*. A situation is possible where the thermodynamic and kinetic flexibilities do not coincide. For example, a polymer with a high thermodynamic chain flexibility (a low value of ΔU) at low temperatures may have a very low kinetic flexibility since the energy of thermal motion of its units under these conditions may prove to be much lower than the potential barrier height.

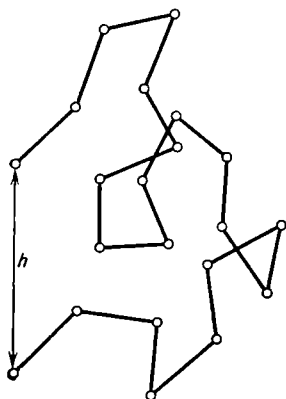


Fig. 1.6. The freely jointed chain model.

One of the first physical models proposed for the description of a number of macromolecular physical properties (and also for the explanation of the flexibility of the polymeric chain) is the model of the freely jointed chain. In such a chain there are no fixed valence angles and the free rotation of the units is possible. A freely jointed chain may have a continuous set of conformations due to the free rotation of the links. A polymeric chain may be characterized not only by its length but also by the distance between its ends (Fig. 1.6). The chain end-to-end distance \bar{h} is usually considered to be a vector drawn from the first atom of the chain to the last one. The value of $|\bar{h}|$ may vary from zero to the maximum value of the chain length equal to zb , where z is the number of repeating units and b is the length of one repeating unit. The value of \bar{h} averaged over all the conformations is equal to zero, since, as a result of thermal motion, all the directions of \bar{h} are equally probable. At the same time the average value of the square of this quantity is different from zero.

In order to find the probability $W(\bar{h})$ that the end-to-end chain distances are within the interval from \bar{h} to $\bar{h} + d\bar{h}$, one can take advantage of the mathematical apparatus and inferences of the theory of diffusion and Brownian motion. It turns out that the probability of this event in a three-dimensional case may be represented (1-3) in the form:

$$W(z, h_x, h_y, h_z) dh_x dh_y dh_z = \left(\frac{3}{2\pi zb^2} \right)^{3/2} \exp \left[-\frac{3h^2}{2zb^2} \right] dh_x dh_y dh_z \quad (1.3)$$

If we turn to spherical coordinates and integrate over all the values of angular coordinates, the distribution function of the absolute

values of h can be written (1) in the form:

$$W(\bar{h}) d\bar{h} = \left(\frac{3}{2\pi z b^2} \right)^{3/2} 4\pi \bar{h}^2 \exp \left(-\frac{3\bar{h}^2}{2z b^2} \right) d\bar{h} \quad (1.3a)$$

The distribution function $W(h)$ in this case turns out to be a Gaussian distribution function. The quantity $W(h)$ signifies the number of possible conformations corresponding to the specified end-to-end distance h of an isolated chain. Thus, the quantity $W(h)$ is the *thermodynamic probability of the chain*. Analysis of expression (1.3a) shows that at $h \rightarrow 0$ and $h \rightarrow \infty$ the value of $W(h)$ tends to zero. Hence, such states are hardly probable. The maximum possible number of conformations is adopted by the polymeric chain at a certain value of h , which corresponds to the maximum of the distribution function $W(h)$. Employing the ordinary rules of averaging, one can show that the mean square end-to-end distance $\langle h^2 \rangle$ is equal to

$$\langle h^2 \rangle \approx \int_0^\infty h^2 W(h) dh = z b^2 \quad (1.4)$$

The above relation holds when the number of repeating units in the chain $z \gg 1$.

Thus, from what has been said above it follows that, as a result of thermal motion, an isolated polymeric chain must become a random coil since this state is the most probable. Indeed, to the most probable value of the square end-to-end distance

$$h_{pr}^2 = \frac{2}{3} z b^2 \quad (1.5)$$

there corresponds the maximum thermodynamic probability of the chain. At $h = h_{pr}$ the macromolecule can assume the largest number of conformations. It is understandable that such a state (corresponding to a random coil) is the most probable. The largest value of h corresponds to an extended chain and can be realized only in a single way. To this case there will correspond a single conformation of the chain. Naturally, the probability of such an event is very low, and in the free state the macromolecule will tend, as a result of thermal motion, to adopt the most probable conformation (a random coil).

Using formula (1.3a), one can find an expression for the entropy of the polymeric chain. Since the entropy is equal to

$$S = k \ln W(h), \quad (1.6)$$

it follows that expression (1.6) can be represented in the form

$$S = C - 3kh^2/2zb^2 \quad (1.7)$$

where C is a constant which does not depend on h ; k is Boltzmann's constant.

Now we can try to elucidate the factor responsible for the fact that polymers in the rubbery state are capable of undergoing large recoverable deformations. This phenomenon (i.e., the rubber elasticity of polymers) is entropic in character. Indeed, the work necessary for the isothermal deformation of the polymer in the rubbery state is equal to its Helmholtz free energy:

$$dA = dF = dE - T dS \quad (1.8)$$

where F is the Helmholtz free energy; E is the internal energy.

The work required for the extension of the sample is given by

$$dA = f dl \quad (1.9)$$

where f is the tensile force; l is the unit elongation of the sample.

Substituting equation (1.9) into (1.8) yields:

$$f = \left(\frac{\partial E}{\partial l} \right)_T = \left(\frac{\partial E}{\partial l} \right)_T - T \left(\frac{\partial S}{\partial l} \right)_T \quad (1.10)$$

Here it is necessary to take into account the fact that the polymer in the rubbery state is practically incompressible and we may neglect the very small change in volume upon deformation. Experiment shows that in polymers in the rubbery state the internal energy is practically independent of the length of the sample, i.e.,

$$\left(\frac{\partial E}{\partial l} \right)_T = 0 \quad (1.11)$$

Hence, the appearance of an elastic force in the polymer, which is in the rubbery state, is due to the change in the entropy:

$$f = -T \left(\frac{\partial S}{\partial l} \right)_T \quad (1.12)$$

Thus, when the entropy of the polymer decreases, which occurs upon extension, the elastic force is increased. In this sense the polymer in the rubbery state is analogous to an ideal gas. Despite the dissimilarity of these substances, in both cases the elasticity has the character of the entropy.

Utilizing formulas (1.12) and (1.7), one can estimate the elastic force that arises upon extension of an individual chain:

$$f = -T \left(\frac{\partial S}{\partial h} \right)_T = \frac{3kT}{zb^2} h \quad (1.13)$$

Thus, the elastic force of the polymeric chain is found to be directly proportional to the end-to-end distance h . Upon extension of such a chain its elasticity increases, and in the unextended state the chain becomes a random coil. A further important property of polymers in the rubbery state is that its elastic force is directly proportional to the temperature. Thus, it is clear that the rubber elasticity of

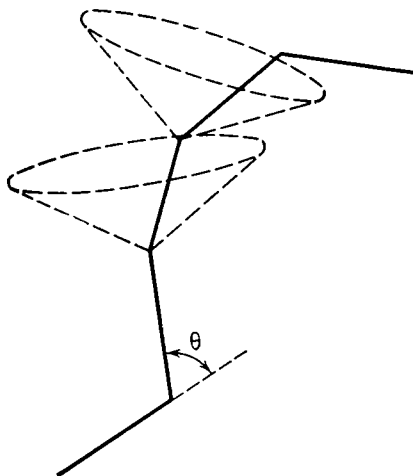


Fig. 1.7. The model of a polymeric chain with fixed valence angles.

polymers is due to the thermal motion of the links, which results from the internal rotation.

It should be noted that the freely jointed chain model is only the first and rather crude approximation. It does not take account of the actual structure of polymeric chains and is insufficient for the description of their behaviour. In polymer chains the valence angles (bond angles) are sufficiently rigidly fixed and the rotation of the links is not free. Let us consider, from this viewpoint, the chain of polyethylene (Fig. 1.7). Let the position of the first two links of the chain be specified.

We denote the angle between the axes of the first and the second link by the letter θ . Then $(\pi - \theta)$ will represent the valence angle between the C—C bonds. This angle is equal to $109^{\circ}28'$. Note that the third link in the chain can no longer occupy an arbitrary position in space. It can only be on the surface of a cone with 2θ . It is obvious that to these possible positions of the link there will correspond different values of the potential energy $U(\varphi)$. The position of the fourth link will be even less definite with respect to the first two links since it can lie on the cone described around each of the positions of the third link. Even less definite with respect to the first two links will be the position of the fifth link and more remote links. Thus, a long chain with fixed valence angles is also able to coil. Obviously, such a chain can be mentally split into statistical elements (segments), whose positions in space are no longer correlated. It is interesting that formulas (1.3) through (1.7) and (1.13) remain to be valid, but in this case the quantity z denotes the number of segments and b the length of the segment.

If the hindered internal rotation and fixed valence angles are taken into account, the expression for the mean square end-to-end distances will differ from that stipulated by formula (1.4). For example, for

a chain with symmetrical pendant side groups (a chain of the type of the polyethylene chain) this expression will have the form:

$$\langle h^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} \cdot \frac{1 + \eta}{1 - \eta} \quad (1.14)$$

where N is the number of monomeric units in the molecule; l is the length of the monomeric unit; θ is the angle complementary to the valence angle; η is the mean cosine of the angle of internal rotation.

In the case of free internal rotation $\eta = 0$ and the chain will be the most flexible; at $\eta = 1$ the chain will be the most rigid. For hindered rotation the mean value of $\eta = \langle \cos \varphi \rangle$ is found from the formula

$$\eta = \langle \cos \varphi \rangle = \frac{\int_0^{2\pi} e^{-\frac{U(\varphi)}{kT}} \cos \varphi d\varphi}{\int_0^{2\pi} e^{-\frac{U(\varphi)}{kT}} d\varphi} \quad (1.15)$$

It is clear that the quantity $\langle h^2 \rangle$ may be treated as a measure of the thermodynamic chain flexibility. It is evident that the lower the value of $\langle h^2 \rangle$ at specified N and l the greater is the chain flexibility. In order to determine $\langle h^2 \rangle$ it is necessary to know η and, hence, the form of the function $U(\varphi)$. The determination of the exact shape of the function $U(\varphi)$ for real macromolecules presents formidable difficulties and is not always realizable. It has, however, been found that it is possible to employ a simplified theoretical approach to the solution of this problem on the basis of the theory of rotational isomerism (conformational theory) proposed in 1951 (1, 4, 5).

1.4. Theory of Rotational Isomerism

The theory of rotational isomerism (1, 4, 5) proposed by Volkenstein treats a polymeric chain as an equilibrium mixture of rotational isomers. The internal rotation is looked upon as rotational isomerism, i.e., the flip of individual units from one conformation to another. In actual fact, apart from such flips, there are also possible thermal fluctuations, which manifest themselves as torsional vibrations with angles of rotation φ corresponding to the minima on the $U(\varphi)$ curve, i.e., about the positions corresponding to the rotational isomers. These fluctuations, however, do not affect the averaged properties of polymeric chains since, by virtue of their random nature, they are mutually compensated.

It has been said above that the curve of $U(\varphi)$, which characterizes the potential energy of internal rotation in a polymer, has, as a rule, several nonequivalent minima. Hence, upon rotations the links of the macromolecule cannot assume any position on the surface of the cone of rotation; they can occupy only those positions which correspond to the minima of the potential energy and are determined

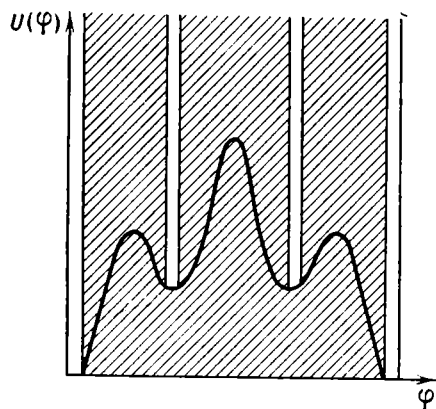


Fig. 1.8. Replacement of the continuous curve of internal rotation $U(\varphi)$ with discrete minima.

by the chemical structure of the polymer. This enables one to replace, in an approximate manner, the $U(\varphi)$ curve by a set of the energies of the rotational isomers produced by the rotation about each of the links of the macromolecular chain. A rotational isomer is characterized by a definite value of the angle of rotation φ and a definite value of the Helmholtz free energy F . In the rotational-isomerism theory the continuous function $U(\varphi)$ is replaced by a finite and small number of narrow slits of different depths (Fig. 1.8). Thus, the continuous function $U(\varphi)$ is replaced by a discontinuous function. This allows us to replace the integration in formula (1.15) in calculating η by summation over a finite number of discrete rotational isomers:

$$\eta = \frac{\sum_{i=1}^n g_i \cos \varphi_i}{\sum_{i=1}^n g_i} \quad (1.16)$$

where n is the number of rotational isomers; g_i is the statistical weight of the i th rotational isomer.

The quantity g_i is defined by the expression

$$g_i = \exp \left(-\frac{F_i}{kT} \right) \quad (1.17)$$

where F_i is the Helmholtz free energy of the i th rotational isomer; k is the Boltzmann constant.

Thus, in the theory of rotational isomerism a linear polymer is regarded as an equilibrium mixture of rotational isomers (conformers), which is realizable within the limits of each particular macromolecular chain.

Let us find the expression for $\langle h^2 \rangle$ in the theory of rotational isomerism. To this end, we substitute Eqs. (1.16) and (1.17) into for-

mula (1.14):

$$\langle h^2 \rangle = Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} \frac{\sum_{i=1}^n g_i (1 + \cos \varphi_i)}{\sum_{i=1}^n g_i (1 - \cos \varphi_i)} \quad (1.18)$$

From relations (1.17) and (1.18) it is seen that in the theory under discussion the quantity $\langle h^2 \rangle$, which characterizes the thermodynamic flexibility of the chain, depends on the temperature and on the values of the Helmholtz free energy of the rotational isomers. In other words, $\langle h^2 \rangle$ depends on the difference in the ordinates corresponding to the minima of the potential energy $U(\varphi)$.

Suppose that the most stable rotational isomer has a Helmholtz free energy F_1 and a statistical weight equal to

$$g_1 = \exp \left(-\frac{F_1}{kT} \right)$$

In this case the statistical weight of any other isomer may be represented in the following form:

$$g_i = e^{-\frac{F_i}{kT}} = e^{-\frac{F_1}{kT}} e^{-\frac{F_i - F_1}{kT}} = g_1 e^{-\frac{\Delta F_i}{kT}}$$

Substituting the expression for g_i into formula (1.16) and cancelling g_1 , we obtain:

$$\eta = \langle \cos \varphi \rangle = \frac{\cos \varphi_1 + \sum_{i=2}^n e^{-\frac{\Delta F_i}{kT}} \cos \varphi_i}{1 + \sum_{i=2}^n e^{-\frac{\Delta F_i}{kT}}} \quad (1.19)$$

Using the value of η , one can also obtain the corresponding formula for $\langle h^2 \rangle$. The most significant point here is that the formulas obtained point to the dependence of the thermodynamically equilibrium state of the chain on the difference in the Helmholtz free energies ΔF and not on the height of the potential barrier. If the difference in the entropies of the rotational isomers is negligibly small, formula (1.19) can then be written in the following form:

$$\eta = \frac{\cos \varphi_1 + \sum_{i=2}^n e^{-\frac{\Delta E_i}{kT}} \cos \varphi_i}{1 + \sum_{i=2}^n e^{-\frac{\Delta E_i}{kT}}} \quad (1.20)$$

where ΔE_i is the difference in the energies of the rotational isomers.

For polyethylene and similar polymers formula (1.20) simplifies and assumes the form

$$\eta = \frac{1 - e^{-\frac{\Delta E}{kT}}}{1 + 2e^{-\frac{\Delta E}{kT}}} \quad (1.21)$$

The values of ΔE and ΔF can be determined by comparing the properties of low-molecular-mass compounds that have an analogous chemical structure. Besides, the value of $\langle h^2 \rangle$ (and, hence, of η) can be determined experimentally in investigations of polymer solutions.

The question of the applicability of the theory of rotational isomerism (conformational theory) to the description of polymers has been considered in detail by M. V. Volkenshtein in his monograph *Configurational Statistics of Polymeric Chains* (1) and in a number of other works (2-5). Volkenshtein has shown that the rotational-isomerism theory is well substantiated for those cases where the minima of the potential energy are separated by energy barriers, which by far exceed kT . If this condition is not observed, the rotational-isomerism theory may be used as an approximate mathematical method which allows one to replace the integration by summation. In this sense the rotational-isomerism (conformational) theory may be regarded as a model mathematical theory.

The existence of rotational isomers (conformers) in polymers has been established experimentally by the methods of infrared spectroscopy. It has been found that for the most important polymers the magnitude of the potential energy barrier significantly exceeds kT . The theory of rotational isomerism has been verified by experiment in studies of the thermomechanical characteristics and deformation of polymers. At present this theory forms the basis for the statistical physics of macromolecules. A systematic treatment of this theory is available in the literature (1, 6, 7).

It should be noted that several years ago an attempt was made (8) to construct the statistical physics of macromolecules without recourse to the concepts of rotational isomers. Almazov and Pavlot-sky (8) have shown that the use of the mathematical apparatus and methods of modern statistical physics enables one to describe the physical properties of macromolecules by taking account of a continuous (and not a discrete) set of their conformations. However, in using this theory for the solution of particular problems (for example, the deciphering of the heredity code) erroneous results have been obtained, which naturally lessens the interest to this method of building up a theory.

References

1. Volkenshtein, M. V., *Configurational Statistics of Polymeric Chains*, Izd. Akad. Nauk SSSR, Moscow, 1959 (in Russian); Volkenstein, M. V., *Configurational Statistics of Polymeric Chains*, Interscience, New York, 1963.
2. Volkenshtein, M. V., *Molecules and Life*, Nauka, Moscow, 1965 (in Russian).
3. Volkenshtein, M. V., *Molecular Biophysics*, Nauka, Moscow, 1975 (in Russian).
4. Volkenshtein, M. V., *Doklady Akad. Nauk SSSR*, 78, 5, 879 (1951).
5. Volkenshtein, M. V., *Zhurn. Fiz. Khim.*, 26, 8, 1072 (1951).
6. Birshtein, T. M. and O. B. Ptitsyn, *Conformations of Macromolecules*, Nauka, Moscow, 1964 (in Russian); Interscience, New York, 1966.
7. Flory, P., *Statistical Mechanics of Chain Molecules*, Academic Press, Wiley-Interscience, New York, 1969.
8. Almazov, A. B. and I. P. Pavlotsky, *The Probabilistic Methods in the Theory of Polymers*, Nauka, Moscow, 1971 (in Russian).

Chapter 2

Modern Concepts of Polymer Structure

The conception that has recently gained wide recognition consists in that the main physical properties of polymers (including their mechanical properties) depend not only on the chemical structure but also on the supermolecular organization (1). It is presumed that the decisive influence on the physical properties of polymers is exerted by their chemical structure, this influence being realized through the physical structure. This conception has been formulated most distinctly in the works of Kargin and his pupils and has been extensively developed. The idea of the effect of the supermolecular structure on the mechanical properties of polymers forms the basis for the so-called "structural mechanics of polymers". We are faced with a rather paradoxical situation: many of the adherents of this conception have gradually come to the conclusion that the basic physical properties of polymers are governed by their supermolecular structure alone. They assume tacitly that the physical (primarily mechanical) properties of polymers do not practically depend (or depend but slightly) on the chemical structure. As a result, among the works devoted to the investigation of polymer structure we find a number of works which are either entirely erroneous or interpret experimental facts incorrectly. The information on polymer structure that we have at our disposal has proved to be rather contradictory, and numerous "experimental" proofs furnished by a number of sensational structural models have been found to be artefacts. There is not too much reliable and indisputable information on the physical structure of polymers.

What is indisputable is that all polymers can be divided into two groups. The first group embraces all polymers that can be produced in the crystalline state; the second group incorporates amorphous polymers.

The criterion for this classification of polymers into two groups is furnished by X-ray diffraction (or electron diffraction). If we have a sharply defined set of reflections (dots, spots, or lines on an X-ray photograph or maxima on diffraction curves), the polymer has a crystalline structure. The X-ray structure analysis of amorphous polymers gives diffuse amorphous halos instead of distinct reflections.

Polymers are evidently characterized by a large number of inter-

mediate stages of the ordered arrangement of chains, i.e., the existence of the various levels of supermolecular organization, which intervene between the crystalline and the completely amorphous (i.e., structureless, disordered) state.

The most important feature of polymers in the crystalline state is that they are not generally composed of crystallites alone; they also contain amorphous regions. In a number of cases, polymer single crystals can be produced by special techniques. Thus, Keller (2) observed single crystals of polyethylene obtained from solution. The single crystals of polyethylene were thin homogeneous layers about 100 Å thick, their shape corresponding to the orthorhombic system characteristic of paraffins. It has been found that single crystals grow by way of formation of spiral platelets along screw dislocations. Polymer single crystals have been observed in isotactic poly-4-methyl pentene-1 and also in polyformaldehyde, whose single crystals were produced by the radiation-induced solid-phase polymerization of trioxane.

All polymer single crystals obtained are, however, very small and the bulk polymer usually consists not only of crystals but also of amorphous (disordered) regions. Therefore, the term "crystalline polymer" in fact means that it is only partially crystalline.

The most "direct" methods of investigation of the structure of polymers are: X-ray structure analysis, electron microscopy and optical microscopy.

2.1. Methods of Investigating Polymer Structure

2.1.1. X-Ray Diffraction

2.1.1.1. Principal Methods of Structure Elucidation

The X-ray structure analysis is based on the phenomenon of diffraction of X-rays by a substance. X-Rays are short electromagnetic waves. In the X-ray diffraction analysis, use is made of rays with wavelengths of 0.5-2.5 Å. If a beam of X-rays falls on a crystal, whose dimensions are of the same order of magnitude as the wavelength, diffraction can occur.

The atoms are distributed in a crystal in such a manner that their arrangement is repeated in three directions. A set of identical point-atoms in space generate a three-dimensional space lattice. The three non-coplanar vectors \vec{a} , \vec{b} , \vec{c} , the repetition of which can produce the entire three-dimensional space lattice of points, are called unit or primitive translations. The parallelepiped built up by application of the three unit translations is called the unit cell. Seven types of

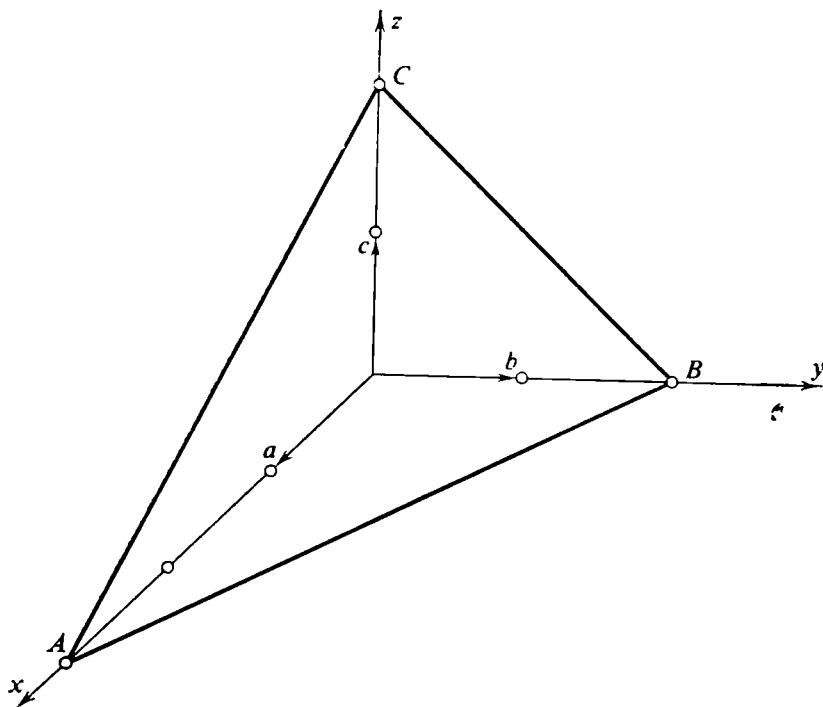


Fig. 2.1. The lattice plane which cuts off the intercepts A , B and C on the coordinates.

unit cell are distinguished: cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, and triclinic. Accordingly, there exist seven crystal systems. Polymer molecules form crystals belonging to all the crystal systems, except the first (the cubic system).

Let one of the lattice points be at the origin and the directions of the three vectors \bar{a} , \bar{b} , \bar{c} be the coordinate axes. Any point of the lattice that has coordinates which are multiples of \bar{a} , \bar{b} , \bar{c} is called a lattice point. The lattice line is a straight line on which the lattice points lie. A crystal plane (a plane which passes through lattice points) is a set of lattice lines lying in a single plane.

Let us consider a lattice plane which cuts the intercepts A , B , C from coordinate origin (Fig. 2.1). If x , y , z are the coordinates of a certain point of the plane, the equation for this plane will have the following form:

$$\frac{x}{A} + \frac{y}{B} + \frac{z}{C} = 1 \quad (2.1)$$

It is obvious that the coordinates x, y, z can be represented in the form:

$$x = ma; \quad y = nb; \quad z = pc \quad (2.2)$$

where $\bar{a}, \bar{b}, \bar{c}$ are the axes of reference.

Substituting formulas (2.2) into Eq. (2.1), we obtain:

$$m \frac{a}{A} + n \frac{b}{B} + p \frac{c}{C} = 1 \quad (2.3)$$

The fractions $a/A, b/B$, and c/C are rational numbers. The ratio of the rational numbers may be replaced by the ratio of integers. Let h, k, l be small integers for which the following condition is fulfilled:

$$\frac{a}{A} : \frac{b}{B} : \frac{c}{C} = h : k : l \quad (2.4)$$

The indices of the unit or reference plane (the Miller indices) are three small whole numbers (h, k, l) which have no common multiplier u and are inversely proportional to the intercepts cut off by the given plane on the axes of reference.

For the plane shown in Fig. 2.1 the Miller indices are equal to:

$$h : k : l = \frac{1}{3} : \frac{1}{2} : \frac{1}{2} = 2 : 3 : 3$$

The position of such a plane in the crystal lattice can be defined with the aid of three numbers— h, k, l . This plane is designated as (233). If one of the Miller indices is equal to zero, the plane intersects the corresponding axis at infinity. This means that the plane is parallel to this axis.

The symbols for the lattice planes in the hexagonal system contain four indices: h, k, i, l . The index i is connected with the indices h and k by the relation $i = -(h + k)$.

The distance d_{hkl} between two neighbouring parallel planes (the interplanar distance) is determined with the aid of the following relations:

(1) for the cubic system

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.5)$$

(2) for the orthorhombic system

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \quad (2.6)$$

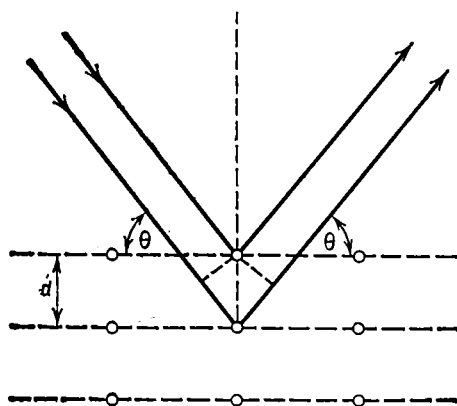


Fig. 2.2. The reflection of X-rays by a family of atomic planes.

(3) for the tetragonal system

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2 \left(\frac{a}{c}\right)^2}} \quad (2.7)$$

For the monoclinic and triclinic systems, which are most typical of a number of polymers, the corresponding formulas have a more complex form.

The intensity and direction of X-rays that have been diffracted by a crystal are recorded by a quantum detector (a Geiger counter or a scintillation counter) or by a photographic technique. The direction of a diffracted X-ray is given by the Wulff-Bragg formula (also known as the Bragg relation):

$$2d_{hkl} \cdot \sin \theta = n\lambda \quad (2.8)$$

where d_{hkl} is the interplanar distance; θ is the Bragg angle (Fig. 2.2); λ is the wavelength of X-rays; n is an integer.

The angle θ is readily determined experimentally: it is equal to the half of the angle between the incident and diffracted rays; λ is always known (for example, for an X-ray tube with a copper anode $\lambda = 1.542 \text{ \AA}$ for the Cu $K\alpha$ radiation); n may be taken to be equal to unity in many cases. Thus, using the Wulff-Bragg formula, one can determine a set of interplanar distances typical of a given crystal, and if we know the crystal system to which it belongs, we can determine the unit-cell dimensions a , b , c by using relations of the types (2.5) through (2.7). If the type of the unit cell is unknown, the determination of the unit-cell parameters is considerably complicated.

In order to elucidate the structure of crystals, various methods are used (3-6). These methods include Laue's method, the rotating crystal method, and the Debye-Scherrer method (the powder technique).

The **Laue method** makes use of polychromatic X-radiation. If we place a single crystal in the path of a beam of X-rays, there will

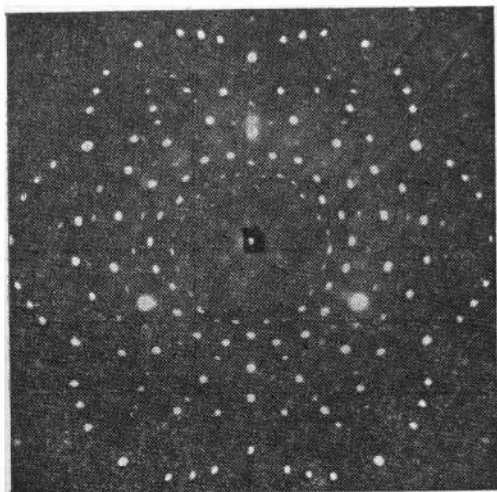


Fig. 2.3. Laue photograph.

always be in it such crystallographic planes (hkl) for which at certain wavelengths of electromagnetic waves ($\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$) Eq. (2.8) is satisfied. An array of spots will be produced on the photographic plate placed behind the crystal under study, as a result of the diffraction of X-rays (Fig. 2.3). Each spot on the Laue photograph has resulted from the interference of the X-rays reflected by a certain family of parallel crystallographic planes. The directions of the X-rays that produce interference spots on the Laue photograph are given by the Bragg formula. The Laue technique allows one to establish the relative disposition of the lattice planes. It is used mainly for the determination of the symmetry elements of crystals and also for the determination of the orientation of poorly faceted crystals.

The **rotating crystal method** has found wide application for structure determinations. In this method, monochromatic X-radiation is employed and the sample to be studied is a single crystal. Since single crystals are not always readily available for all polymers and the size of the single crystals obtained is too small, in investigations of polymer structure use is made of oriented, maximally crystallized polymer films or fibres. When the crystal is rotated about some axis, the X-rays directed at right angles to this axis are found, at a certain moment of time, to be in such a position relative to some crystallographic planes for which the Bragg relation is satisfied. In this case, there appears a diffracted X-ray which gives rise to a reflection (a diffraction spot) on a cylindrical photographic film, whose axis coincides with the rotation axis of the crystal. On the cylindrical film the reflections are arrayed in a series of lines (known as layer lines) perpendicular to the axis of rotation. The layer line passing through the trace left from the primary beam of X-rays is called

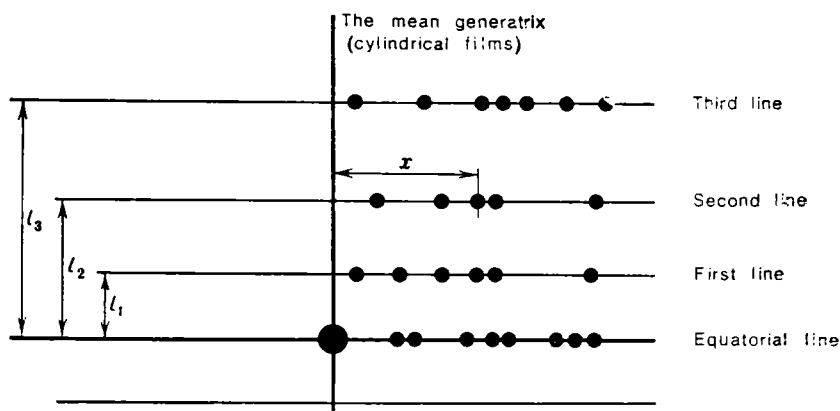


Fig. 2.4. Schematic representation of the rotation photograph of a single crystal.

the zero layer line. The arrangement of the other layer lines is shown in Fig. 2.4. The separation of the layer lines depends on the distance between the identical scattering centres arrayed along the axis of rotation of the crystal. The repetition distance I in this direction is given by the formula

$$I = n\lambda / \sin \mu_n \quad (2.9)$$

where λ is the X-ray wavelength; n is the number of the layer line (for the zero layer line $n = 0$); μ_n is determined by the formula $\tan \mu_n = l_n/A$, where l_n is the distance between the n th and zero layer lines, and A is the distance between the sample and the photographic film.

From three rotation photographs obtained for three different crystallographic directions chosen in some special way one can find three repeat distances and, hence, to determine the shape and dimensions of the unit cell. Then the indexing of the photograph is carried out, i.e., the Miller indices (hkl) of the reflecting planes are found. A set of the indices thus obtained and the absence (extinction) of some of them allow one to determine the space group of the crystal.

In the X-ray structure analysis of polymers, so-called fibre diagrams are obtained by using oriented samples. In the case of the uniaxial orientation of a crystalline polymer, when the same axis in all the crystallites is oriented in a single direction and the rotations about it are arbitrary, an axial texture is obtained. The X-ray photograph of the polymer, which has an axial texture, is analogous to the rotation photograph. The difference is that it is not necessary to rotate the sample in order to obtain a fibre photograph. The zero layer line on the fibre photograph is called the equator and the line perpendicular to the equator and passing through the trace left from the primary beam is called the meridian. If the primary beam is

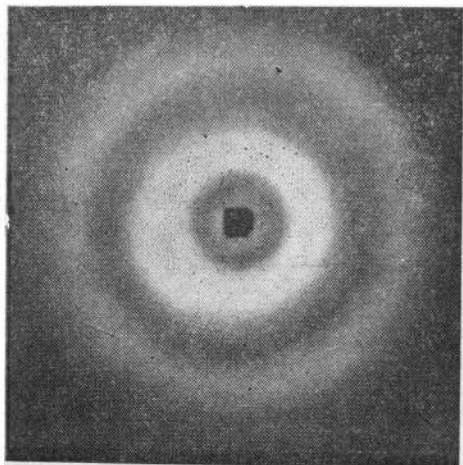


Fig. 2.5. X-Ray photograph of amorphous polyethylene terephthalate on a flat film.

directed so that it is normal to the fibre axis (the orientation direction), then the reflections will be arrayed symmetrically with respect to both the equator and the meridian.

Reflections that appear on the equator of the photograph are the result of the reflection from a set of planes parallel to the fibre axis. For example, the fibre photograph of oriented well-crystallized polycapramide, whose crystals form a monoclinic unit cell, shows the reflections (002) and (200) on the equator. These reflections are produced upon reflection of X-rays from the (002) and (200) planes parallel to the axis "*b*" which coincides with the fibre axis.

It is clear that the reflections that appear on the meridian of the fibre photograph correspond to the reflection of X-rays from the crystallographic planes perpendicular to the fibre axis. But for the reflection corresponding to the angle θ to be obtained on the meridian of the photograph, it is necessary that the angle between the primary beam and the fibre axis be $90^\circ - \theta$.

The structure of polycrystalline materials (almost all crystalline polymers are such materials) is investigated by means of the **Debye-Scherrer powder method**. The essence of this method is as follows. A beam of monochromatic X-radiation is incident on a polycrystalline sample (a powdered sample); there will always be a proportion of small crystals in the sample that are under the conditions for which the Bragg formula is satisfied. Since these tiny crystals (crystallites) are oriented randomly in the sample, upon reflection from each set of parallel planes inside such crystallites for which formula (2.8) is satisfied a cone of diffracted X-rays is produced. The axis of this cone coincides with the direction of the primary beam. When a flat photographic film is placed behind the sample in the path of an X-ray beam perpendicular to the beam a series of rings will be produced (Fig. 2.5).

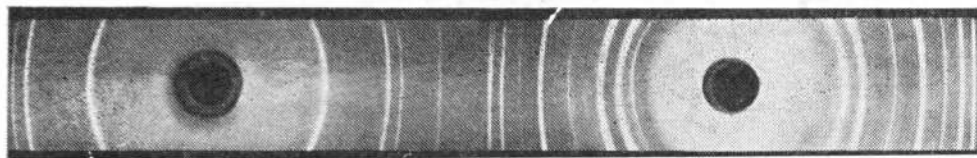


Fig. 2.6. Debye photograph.

If a cylindrical strip of photographic film surrounds the sample and a beam of X-rays is perpendicular to the axis of the cylinder, a series of crescents or arcs will be formed on the photographic film which are symmetrical with respect to the primary beam. The photograph thus obtained is known as the Debye powder photograph (Fig. 2.6). By scanning the powder photograph photometrically along the equator we can obtain information on the intensity distribution of the diffracted X-rays as a function of the angle θ (the Bragg angle). The dependence of the intensity of diffracted X-rays on the angle θ can also be obtained directly through the use of a Geiger counter (or a scintillation counter) in the X-ray diffractometer. Such an X-ray diffraction pattern is shown in Fig. 2.7 for a highly crystalline low-pressure polyethylene. By measuring the distance between the symmetrical arcs on the Debye powder photograph (or the spacing between the corresponding symmetric maxima on the diffraction pattern) we can readily find the angle 2θ and then calculate the interplanar distances d by means of the Bragg formula.

The elucidation of the detailed structure of polymers by X-ray diffraction methods is a rather complicated task. This is because one has to use polycrystalline samples, which always contain amorphous

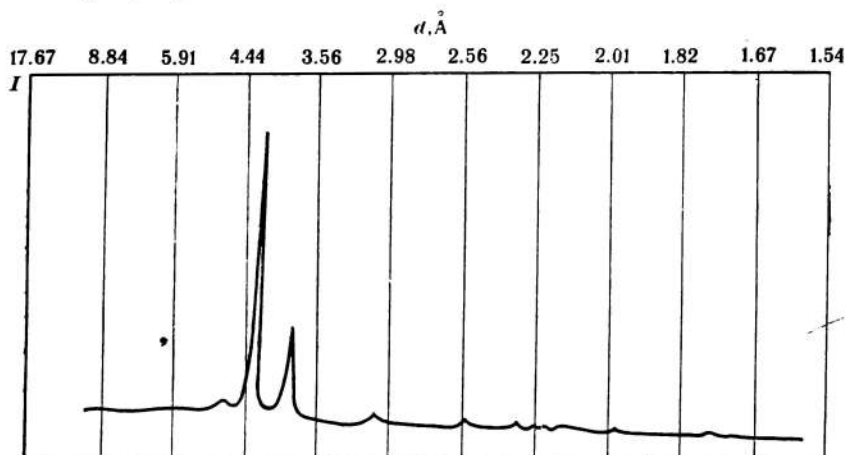


Fig. 2.7. The X-ray diffraction curve of low-pressure polyethylene.

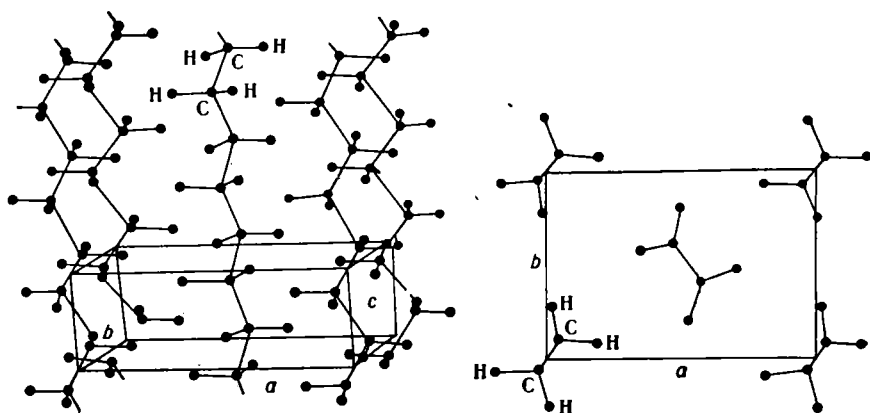


Fig. 2.8. The arrangement of chains in the unit cell of polyethylene.

regions, instead of single crystals which are too small for the X-ray diffraction analysis. The X-ray photographs of even highly crystalline polymers contain a considerably smaller number of reflections than those of low-molecular-mass solids. Besides, the presence of an amorphous halo and the reflections strongly diffused because of the small size of crystallites are the factors that considerably complicate the determination of the structure of polymers.

Usually, for the crystalline structure to be studied one makes use of well crystallized samples. Having obtained the fibre photograph of the polymer prepared in this way, one can find the length of the repeat unit if one of the repeat distances is known. Further, knowing the chemical structure of the polymer, we can determine the configuration of the macromolecule.

A typical example of a polymer crystal is the crystalline lattice of polyethylene (Fig. 2.8). The polyethylene chain forms in space a planar zig-zag. The distance between two adjacent carbon atoms in the polymeric chain is 1.54 \AA and the valence angles formed by the C—C—C bonds are about 109.5° . The macromolecules of polyethylene form an orthorhombic unit cell which is characterized by the following parameters: $a = 7.40 \text{ \AA}$, $b = 4.93 \text{ \AA}$, and $c = 2.534 \text{ \AA}$. The polymeric chains in polyethylene crystals are arranged parallel to one another and are directed along the axis "c". The hydrogen atoms are arranged in planes parallel to the plane "ab" of the unit cell.

Of great importance for the solution of the problems in polymer physics is the determination of structure parameters such as the degree of crystallinity, the size and orientation of crystallites, and the large repeat distance.

2.1.1.2. Determination of Crystallinity

Numerous investigations show that practically all crystalline polymers contain amorphous regions. The existence of amorphous regions leads to the appearance of amorphous halos in addition to discrete reflections on the X-ray diffraction patterns of crystalline polymers. In order to estimate the share of the volume (or mass) of the crystalline regions in the entire polymer, use is made of the concept of the degree of crystallinity.

Let us consider a polymer sample of mass m . Let the mass of all the crystalline regions in this sample be m_{cr} and the mass of all the amorphous regions m_{am} . Then $m = m_{cr} + m_{am}$.

From this it follows that

$$\rho V = \rho_{cr} V_{cr} + \rho_{am} V_{am} \quad (2.10)$$

where ρ is the density; V is the volume.

Dividing both parts of formula (2.10) by V , we obtain:

$$\rho = \frac{V_{cr}}{V} \rho_{cr} + \frac{V_{am}}{V} \rho_{am} \quad (2.11)$$

It is obvious that $V_{cr}/V = \kappa$ represents the relative (volume) fraction of crystalline regions in the polymer. The quantity κ , which is called the degree of crystallinity (or, simply, crystallinity), may assume values ranging from 1 (a completely crystalline polymer) to 0 (a completely amorphous polymer). The quantity $V_{am}/V = 1 - \kappa$ indicates the relative volume occupied by the amorphous regions.

Formula (2.11) may be written as follows:

$$\rho = \kappa \rho_{cr} + (1 - \kappa) \rho_{am} \quad (2.12)$$

Having determined the densities of the crystalline (ρ_{cr}) and amorphous (ρ_{am}) regions, we can determine, using formula (2.12), the degree of crystallinity of a polymer if its density ρ is known. Apart from the degree of crystallinity by volume, there also exists the degree of crystallinity by mass. The volume of a sample of a crystalline polymer can be defined as

$$V = V_{cr} + V_{am} \quad (2.13)$$

Since $V = m/\rho$, then formula (2.13) may be written in the following form:

$$\frac{1}{\rho} = \kappa \frac{1}{\rho_{cr}} + (1 - \kappa) \frac{1}{\rho_{am}} \quad (2.14)$$

where $\kappa = m_{cr}/m$ is the "mass" ("weight") degree of crystallinity.

Formula (2.14) is sometimes written with the specific volume v being introduced instead of $1/\rho$:

$$v = \kappa v_{cr} + (1 - \kappa) v_{am} \quad (2.15)$$

Obviously, the mass ($\bar{\kappa}$) and volume (κ) degrees of crystallinity do not coincide since $\bar{\kappa}$ usually exceeds κ :

$$\bar{\kappa} = \frac{\rho_{cr}}{\rho} \kappa$$

There exist various methods for the determination of the degree of crystallinity. It can be evaluated from density measurements, using thermophysical methods and also the methods of nuclear magnetic resonance (NMR) and infrared spectroscopy (IR spectroscopy), and X-ray diffraction methods. The crystallinity values obtained for the same polymer by different methods sometimes do not coincide. This discrepancy is often accounted for by the fact that these different methods deal with quite different quantities which are only indirectly related to the degree of crystallinity κ . For example, the NMR method determines the "dynamic" degree of crystallinity defined as the ratio of the number of fixed links to the total number of links in a polymeric sample. It is evident that the "dynamic" degree of crystallinity thus found cannot be regarded under certain conditions (e.g., at temperatures lower than the glass-transition temperature of the amorphous layer) as the true degree of crystallinity. Another factor responsible for the discrepancy in the determination of κ is a deliberately incorrect measurement of this quantity; the precise determination of the degree of crystallinity is sometimes a very laborious procedure.

But there are also difficulties of objective nature in measurements of κ . They are associated with the necessity of knowing the quantities ρ_{cr} and ρ_{am} . While the density of crystallites, ρ_{cr} , can be determined through the use of X-ray data, the evaluation of the density of the amorphous regions, ρ_{am} , is sometimes a very formidable task. This is because only a relatively small number of crystalline polymers (polyethylene terephthalate, polytrifluorochloroethylene, polytetrafluoroethylene) can be produced in the amorphous state, in which the density ρ_{am} is readily measured. For many crystalline polymers the determination of ρ_{am} is carried out by the extrapolation of the temperature dependence of the density of the melt to room temperature. Thus, the simplest method of determination of κ based on density measurements can be used only if the quantities ρ_{am} and ρ_{cr} are known.

The degree of crystallinity is determined most reliably by the X-ray method. There are various procedures for crystallinity determinations which make use of the scattering of X-rays in polymers.

Since apart from discrete reflections, the X-ray diffraction pattern also shows an amorphous halo (the inner ring), it is usually presumed that the integral intensity of crystalline reflexions is directly proportional to the mass fraction of crystalline regions, and the integral intensity of the amorphous halo is proportional to the mass

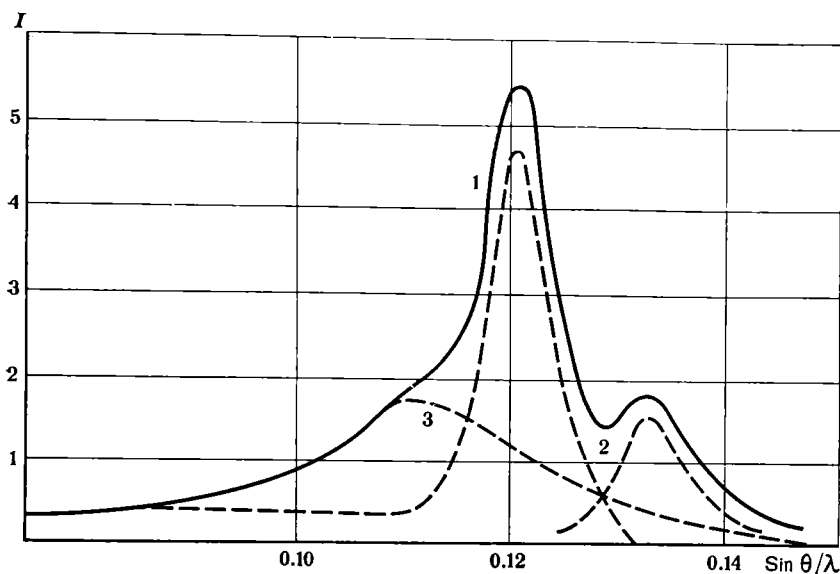


Fig. 2.9. The curve showing the distribution of X-ray intensity of diffraction by polyethylene:

1—resultant curve; 2—dispersion curve for crystallites; 3—dispersion curve for amorphous regions.

fraction of amorphous regions. Therefore, the curve of the intensity of X-rays scattered by a crystalline polymer is resolved into several curves (depending on the number of reflexions on the X-ray photograph) which characterize the scattering by the crystalline and amorphous regions. The area under these curves is proportional to the integral scattering intensity of X-rays. By measuring these areas one can determine the degree of crystallinity with respect to the integral intensities corresponding to the scattering of X-rays by the crystallites and amorphous regions. This method can be realized only for those polymers for which we can single out the integral intensity of the amorphous halo. A typical example in this respect is polyethylene; the intensity distribution curve for this polymer is shown in Fig. 2.9.

It should be remarked that the determination of the degree of crystallinity, like any quantitative X-ray measurements, requires that a number of corrections be introduced and monochromatic X-radiation be used.

The X-ray structure analysis usually makes use of the $K\alpha$ radiation. However, apart from the $K\alpha$ line, the X-ray spectrum also contains the $K\beta$ line, whose intensity is several times lower. In order to suppress the $K\beta$ line, filters are used, which almost completely cancel this line. For example, if the X-ray tube has a copper anode, a nickel foil is used to suppress the $K\beta$ radiation. Apart from the charac-

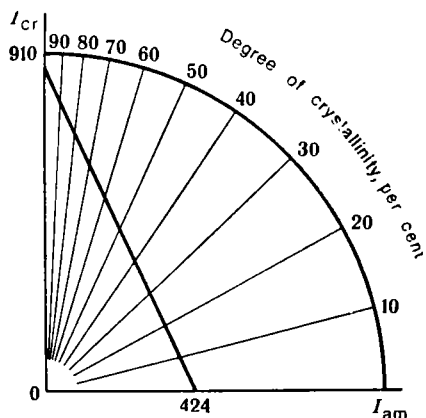


Fig. 2.10. A nomographic chart for determination of the degree of crystallinity of polyethylene by the Hermans-Weidinger method.

teristic radiation, the X-ray spectrum always contains a certain fraction of "white" (continuous) radiation. This white radiation may lead to the formation of an amorphous halo that has nothing to do with the structure of the polymer, the broadening of the line and to the reinforcement of the background below the reflections. All these factors naturally can distort the results of measurements of the degree of crystallinity by the X-ray method. There exist various methods of monochromatization of X-radiation. The technique most frequently employed in polymer investigations is the Ross twin-filter method (7, 8).

The degree of crystallinity of polymers has been determined in recent years by the procedure suggested by Hermans and Weidinger (9, 10). This method requires the use of several samples of the same polymer possessing different crystallinities. If it is necessary to determine \bar{x} in a single sample, the sample is exposed at different temperatures (usually, above room temperature), which results in a change in crystallinity. Having obtained a series of diffraction curves corresponding to samples having different crystallinities, one selects the intensity I_{cr} of one or more reflections proportional to the crystalline content. Then, over a certain range of angles θ a portion of the amorphous halo is selected, which depends on the amorphous content. The intensity of this portion of the amorphous halo, I_{am} , is assumed to be directly proportional to the relative fraction of amorphous regions in the polymer. Having obtained a series of values of I_{cr} and I_{am} for samples of the same polymer which have different (unknown) degrees of crystallinity, we can construct a plot of I_{cr} against I_{am} (Fig. 2.10). If the method is carried out correctly, the graph of I_{cr} versus I_{am} obtained is a straight line. The point of intersection of this straight line with the ordinate corresponds to the value of I_{cr} for a completely crystalline sample ($\bar{x} = 100$ per cent), and the point of intersection of the straight line of I_{cr} versus I_{am} with the ab-

scissa corresponds to the I_{am} value for a completely amorphous sample. Dividing the $I_{\text{cr}} = f(I_{\text{am}})$ straight line into 100 equal parts and measuring the I_{cr} and I_{am} values of the sample, it is not difficult to determine its degree of crystallinity by using the graph plotted. A special feature of the Hermans-Weidinger method is that it can be used to measure not the integral intensities but only the values of I_{cr} and I_{am} which are proportional to the amounts of crystalline and amorphous material present.

2.1.1.3. Determination of the Crystallite Size

The investigation of crystalline polymers has shown that the diffraction maxima are broader (more diffuse) for these polymers than those for low-molecular-mass substances. The broadening of diffraction maxima on X-ray diagrams is usually associated with a decrease in the crystallite size. It is known that the half-width of the diffraction line "B" is related in the following way to the crystallite size L :

$$L = \frac{K\lambda}{B \cos \theta} \quad (2.16)$$

where K is a coefficient which depends on the shape of the crystallite (if the crystallite shape is unknown, then it is usually assumed that $K = 0.9$); θ is the Bragg angle; B is the half-width of the line (the distance between the points at which the intensity is half the maximum intensity).

It should be noted here that the linewidth on the diffraction curve is associated not only with the crystallite size. It may also be due to the natural linewidth (determined by the width of the spectrum of the characteristic radiation) and also to the "instrumental" linewidth, which is determined by the geometrical conditions of exposure.

In order to obtain a more accurate value of the half-width of the line, the X-ray photograph of a reference substance (usually, a single crystal) is taken. On the diffraction curve for this reference substance, which has large crystallites, the linewidth b_{ref} is no longer dependent on the crystallite size and is determined only by the exposure conditions and the natural linewidth. Thus, having determined experimentally the linewidth β_{exp} for the polymer sample under examination, one can find the value of B :

$$B = \sqrt{\beta_{\text{exp}}^2 - b_{\text{ref}}^2} \quad (2.17)$$

Then, the crystallite size L is determined from formula (2.16). Usually, the values of L are found from the half-width of several reflections, following which the value of L_{av} is calculated. In investigations on oriented crystalline polymers, the half-width of re-

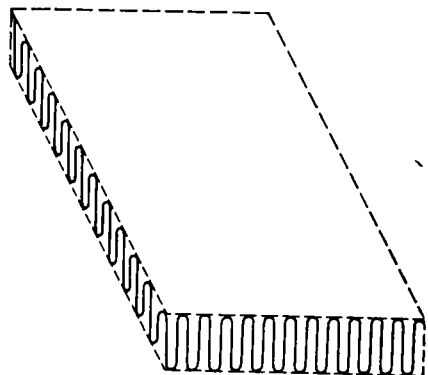


Fig. 2.11. Chain folding in a polymer single crystal.

flections located on the equator of the X-ray diagram can be used to determine the average crystallite size in the direction perpendicular to the fibre axis. From formula (2.16) it follows that the decrease in the crystallite size leads to an increase in the linewidth on the X-ray diagram and to a complete diffuseness and then even to the disappearance of the lines corresponding to large angles θ .

The crystallite size for the majority of crystalline polymers usually ranges from 50 to 500 Å. In a number of crystalline polyolefins (polyethylene, polypropylene) that form lamellar crystals the lamellar thickness (one of the parameters that characterize the crystallite size) is 100-150 Å. If we take into account that the length of the polymer chain is about 10^4 Å, it turns out that the crystallite size is several orders of magnitude smaller than the chain length. In this connection, the conclusion that the crystallites in flexible-chain polymers are formed by chain folds seems to be quite natural (Fig. 2.11).

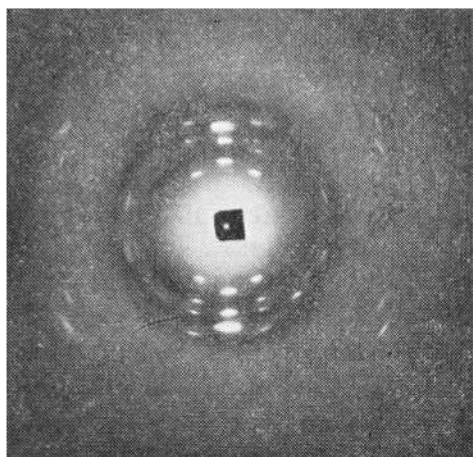
It is necessary to take into account that the crystallite size L is deduced from formula (2.16) only at a more or less accurate approximation. Apart from the small crystallite size, the broadening of the lines on the X-ray diagram is also caused by other factors, say lattice imperfections.

2.1.1.4. Determination of the Orientation of Crystallites

One of the parameters that characterize the structure of polymers is the degree of orientation of crystallites (in crystalline polymers) or polymeric chains (in amorphous polymers). Oriented polymers—in the form of fibres, films, articles produced by pressure casting, extrusion, etc.—are widely used in modern technology and in the home.

The orientation of polymer samples can be deduced from X-ray diffraction patterns recorded on flat photographic film. The X-ray diffraction pattern of an isotropic sample, which is devoid of any

Fig. 2.12. The X-ray photograph of uniaxially oriented annealed polyethylene terephthalate (the X-ray beam is perpendicular to the direction of drawing).



orientation, shows continuous Debye circles (Fig. 2.5). If the sample is oriented, it is placed so that the axis of orientation is perpendicular to the incident X-ray. On the flat photographic film placed behind the oriented sample there appear arcs instead of Debye circles (Fig. 2.12), and in the case of strong orientation spots are produced. The photometric measurement along the arcs obtained shows that the intensity of the diffracted X-radiation is distributed randomly along the azimuth. This means that there exists a certain distribution of crystallite axes with respect to the fibre axis. A more detailed picture of the polymer texture can be obtained if one more X-ray pattern of the oriented sample is recorded on flat film: the sample is placed so that the supposed major axis of orientation coincides with the X-ray beam direction. The continuous circles on the diffraction pattern of the oriented specimen point to the axial texture of the polymer (the uniaxial orientation of the crystallites). But if the X-ray diagram of the oriented sample, recorded so that its axis of orientation is parallel to the beam of X-rays, contains arcs instead of continuous circles, this means that the sample has an axial-planar texture. Such a texture appears, for example, when the polymer film is stretched in two mutually perpendicular directions.

A complete picture of the orientation of crystallites can be obtained if one constructs so-called pole figures (7, 8). This method, however, has not found wide application in the study of the orientation of polymers because it is very time-consuming.

For the orientation of polymers to be evaluated quantitatively, use is made of the orientation function (the orientation factor according to Hermans) (11). The orientation factor α is defined by the formula

$$\alpha = \frac{1}{2} \{3 \langle \cos^2 \tilde{\theta} \rangle - 1\} \quad (2.18)$$

where $\tilde{\theta}$ is the angle of deflection of the direction of interest in the lattice from the axis of orientation.

For an isotropic sample $\langle \cos^2 \tilde{\theta} \rangle = 1/3$ and $\alpha = 0$. For an ideally oriented sample, $\langle \cos^2 \tilde{\theta} \rangle = 1$; $\theta = 0$ and $\alpha = 1$. The fibre axis does not necessarily coincide with the axis of the polymer chain.

For example, in polyethylene terephthalate even at a maximum degree of orientation the angle between the macromolecular axis and the fibre axis is 5° . The determination of the orientation function by the X-ray method is a rather complicated task. The mean angle of deviation of the direction under study from the axis of orientation $\langle \tilde{\theta} \rangle$ is determined by the X-ray technique considerably more simply.

The quantity $\langle \tilde{\theta} \rangle$ is determined most simply with the aid of an X-ray diffractometer. The angle of deviation of the lattice axis, lying in a plane defined by the Miller indices and giving a reflection characterized by the Bragg angle θ , from the axis of orientation can be found from the following formula (7, 8):

$$\cos \tilde{\theta} = \cos \Psi \cdot \cos (\theta - \Phi) \quad (2.19)$$

where θ is the Bragg angle; $\tilde{\theta}$ is the angle of deviation of the lattice axis chosen from the axis of orientation; Φ is the angle between the normal to the plane of the sample under study and the direction of the incident beam; Ψ is the angle equal to the half-width of the curve of the azimuthal intensity distribution.

If the angle $\tilde{\theta}_m$ is to be determined, the specimen is placed in the diffractometer so that the angle $\Phi = 0$ or $\Phi = \theta$. The X-ray quantum counter is fixed at an angle of 2θ , which corresponds to one of the maxima on the diffraction curve. Then, the specimen of the oriented polymer under study is rotated in its plane and the Ψ_m value is found from the half-width of the azimuthal intensity distribution curve recorded automatically. After this, the angle $\tilde{\theta}_m$ is calculated from formula (2.19). If $\Phi = 0$, then $\cos \tilde{\theta} = \cos \Psi$.

In the case of a biaxially oriented polymer, the determination of the quantitative characteristics of orientation naturally becomes complicated.

2.1.1.5. Small-Angle X-Ray Scattering

Large structural inhomogeneities cannot be detected by ordinary X-ray diffraction methods if the Bragg angles are found to be smaller than 2° . Indeed, from the Wulff-Bragg formula it follows that

$$\sin \theta = \frac{n\lambda}{2d} \quad (2.20)$$

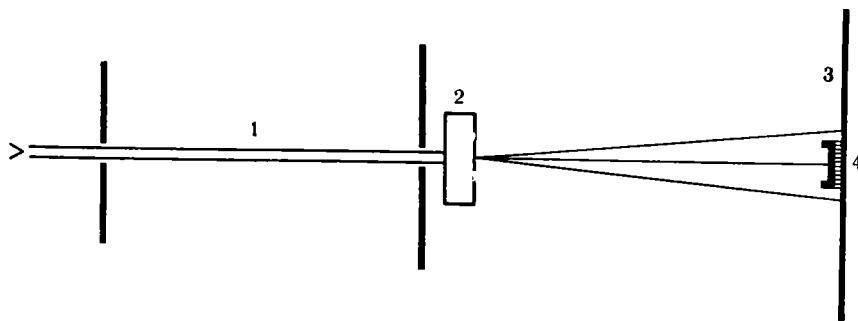


Fig. 2.13. Diagram of an apparatus for small-angle X-ray scattering: 1—collimator; 2—sample; 3—photographic film; 4—beam catcher.

Since in the investigation of polymers n is usually equal to unity and $\lambda = 1.54 \text{ \AA}$ (an X-ray tube with copper radiation), then it is evident that to the diffraction of X-rays by large structural units (large d values) there must correspond small values of θ . The diffraction maxima corresponding to small angles ($\theta < 2^\circ$) cannot, however, be detected by ordinary X-ray methods since they will be superimposed by the intensive diverging primary beam.

The diffraction by large structural units can be observed by using the apparatus and methods devised specifically for the study of small-angle X-ray scattering (SAXS). The small-angle X-ray scattering signifies the scattering over an angular range of several minutes to 2° .

The scattering of X-rays at very small angles is usually observed on the apparatus shown schematically in Fig. 2.13. A narrow monochromatic beam of X-rays incident on the sample 2 under study is picked out with the aid of a collimator 1. Placed at a considerable distance (20-50 cm) behind the sample is photographic film 3. The narrow catcher 4 prevents the primary beam from striking photographic film (which would lead to the appearance of much fogging). Sometimes counters are used instead of photographic film to record small-angle scattering.

Small-angle X-ray diagrams usually show either an intensity maximum (a small-angle reflection) or a monotonic decrease in the intensity of scattered X-rays with increasing angle θ . The quantity d , which is called in this case the large repeat distance, can be calculated from the angle θ corresponding to a small-angle reflection with the aid of formula (2.8). A large repeat distance is observed in many crystalline polymers; it varies from polymer to polymer from several hundreds to several thousands of angströms.

In investigations of oriented crystalline polymers the small-angle reflection is usually observed on the meridian of the X-ray diffraction pattern. It is presumed that the large repeat distance in this

case is determined by the sum of the sizes of the crystallites and the amorphous layer along the axis of the oriented polymeric fibre or film. Employing small-angle X-ray scattering, one can obtain important information about the size, shape and orientation of crystallites and amorphous regions in polymers.

2.1.2. Electron Microscopy

One of the most frequently used and simple methods of investigation of the structure of polymers is optical microscopy. The maximum resolving power of the optical microscope is, however, $\delta \approx \lambda/2$ (where λ is the wavelength of visible light). For visible light with a wavelength of 5000 Å the resolving power of the optical microscope is 2500 Å, and the useful amplification is about 1000. The maximum resolving power of the optical microscope is limited by the diffraction of light by the objects under study which occurs when the light wavelength is of the same order as the dimensions of the object.

The use of the wave properties of electrons in the electron microscope allows one to produce shorter wavelengths and thereby to sharply increase the resolving power of the microscope. The de Broglie wavelength, which characterizes a beam of electrons moving at an accelerated velocity under the influence of the potential difference U , is equal to

$$\lambda = 12.25/\sqrt{U} \quad (2.21)$$

where λ is the de Broglie wavelength in angströms; U is the potential difference in kV, under the influence of which the electron gains its velocity.

With an accelerating voltage of 100 kV, which is typical of modern electron microscopes, the wavelength $\lambda = 0.04$ Å. The resolving power of the best modern electron microscopes is, however, practically lower by two orders and is 1-5 Å. The instruments put out serially usually have a resolving power of about 5 Å and a magnification of 2×10^5 to 2×10^6 . The image of micro-objects in the electron microscope is seen with the aid of a special screen, which becomes fluorescent under the impact of electrons, or is photographed. Usually, the electron microscope is used to study the picture obtained when the electrons are passing through a thin layer (film) of a substance.

In investigations of polymers, use is made of thin films deposited from solution or thin sections produced with the aid of the ultramicrotome. However, under the influence of rapidly flying electrons the structure of the polymer is destroyed, the films melt and the polymer undergoes degradation. Therefore, the polymer structure observed under the electron microscope may differ from the structure that exists in the specimen unirradiated by electrons. Besides, the bulk

structure of the polymer can strongly differ from the structure of the film obtained from solution.

A further difficulty in the investigation of polymers by means of the methods of electron microscopy is associated with the fact that the densities of the ordered and disordered regions in polymers differ little (usually, by no more than 10 per cent), which does not allow one to reveal reliably and uniquely the structure of the polymer on direct irradiation of the polymer sample.

In this connection, the method that has found extensive application in the investigation of polymers by means of electron microscopy is the one in which not the sample itself but its replica (i.e., the imprint of the surface of the specimen under study) is observed under the microscope. When metals are to be investigated, a thin section cut off from the specimen is subjected to etching. Polymer samples are sometimes prepared in a similar way. Etching is usually effected in the vapour of organic solvents, which have a stronger effect on the disordered, amorphous regions. The polymer sample is then placed in vacuum and a thin carbon or quartz film (replica) is deposited onto the section. The thickness of such a structureless replica, which reproduces the surface relief of the specimen, is usually several tens of angströms. To increase the image contrast of the replica, it is shadowed. To this end, a thin layer of a metal with a large atomic number in the Mendeleev Table (Cr, Pt, etc.) is deposited onto the replica at a certain angle.

So, not the polymer sample but the replica made from its surface is observed under the microscope. The resolving power of a well prepared carbon replica usually does not exceed 10 Å.

It is necessary to note that upon etching of the polymer sample certain structural changes may occur in it and the photographs obtained with the electron microscope may show a structure which is not at all typical of the polymer being examined. Phenomena of this kind are ordinary artefacts, which have been repeatedly arisen in the investigations of polymers by the methods of electron microscopy.

Replicas have recently most often been made from cleavages. The polymer under study is cooled down to very low temperatures (for example, it is dipped into liquid nitrogen, the temperature of which is -196°C) and then is cleaved. Then, a replica is taken from the cleaved surface and then observed under the electron microscope. This method seems to be flawless at first glance. However, large stresses can be concentrated on the cleavage surface, which may lead to a certain anisotropy of a number of properties. As a result, artefacts may appear when replicas are taken from the cleavage and observed under the electron microscope. The use of electron microscopy for the investigation of the structure of polymers requires a high skill on the part of the investigator who applies this method.

The electron microscope can be used to observe individual macromolecules, to study the supermolecular structure and to see polymer single crystals. It is with the aid of electron microscopy that the spherulites, fibrils, globules and other elements of the supermolecular structure have been studied in detail.

2.2. The Structure of Crystalline Polymers

An important feature of crystalline polymers is that they consist not only of crystalline but amorphous regions as well. It is necessary to remember that the concept of the structure of a crystalline polymer as an assembly of distinct phases is an idealization. As a matter of fact, the crystalline and amorphous regions are separated by portions with an intermediate degree of ordering. As a rule, there is no sharp borderline between the crystalline and amorphous regions. This is associated not to a small degree with the fact that one macromolecule may run through several crystallites and amorphous regions. The existence of such two-phase chains is a characteristic feature of crystalline polymers. It is exactly such chains that are eventually responsible for the strength of polymers; they are taking the main part of loading stresses upon deformation of the polymer.

It is sometimes believed that a crystalline polymer may be regarded as an amorphous matrix in which small crystallites are randomly distributed. Obviously, such a model is unsuitable for highly crystalline polymers in which the crystallinity is 70-90 per cent. It will be more natural to treat a crystalline polymer as a certain (sufficiently imperfect) crystalline lattice in which the voids are filled with amorphous matter (12). The role of amorphous regions may be played by sites saturated with crystal defects, kinked and jogged chains which form chain-folded crystals, etc.

Crystalline polymers are characterized by a certain variety of structural units corresponding to the various levels of the supermolecular organization.

Below are given data (13) on the structural units and their sizes:

	Minimum size, Å	Maximum size, Å
Molecules	2-5	10^3 - 10^5
Crystallites	20-100	100-500
Crystallites with amorphous matter	200-1000	40-1000
Single crystals	100	10^4 - 10^5
Fibrils in spherulites	10^3 - 5×10^4	10^5 - 10^6
Spherulites	—	10^5 - 10^6 upwards

The principal structural unit of a crystalline polymer is a crystallite. More complex supermolecular structures result from the various combinations of crystallites. It has been thought for a long time

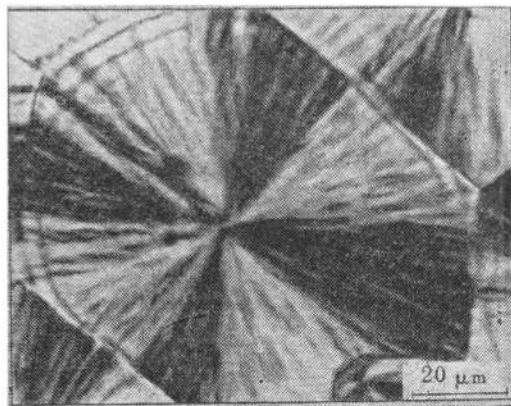


Fig. 2.14. A polymer spherulite.

that crystallites in polymers are formed by straightened macromolecular chains. At present it is believed that such a chain morphology in crystallites is most typical of rigid-chain polymers. Flexible-chain polymers probably most often form folded crystals upon crystallization. Figure 2.11 shows how such a crystal is produced by folded macromolecular conformations in a crystalline lamella. The concept of crystal lamellae, whose thickness is determined by the fold length of the polymer chain, is one of the important concepts in modern physics of polymers. The concept of the folding of polymer chains allows one to account for a number of specific features in the behaviour of polymers. Polymer single crystals observed experimentally are, as a rule, formed as a result of the folding of macromolecules. The morphology of polymeric chains that form crystals is considered in detail in the literature (12-15).

The largest and most complex form of the supermolecular structure is spherulites. Spherulites in the form of beams of radial lines emerging from a single centre can be observed in many crystalline polymers under the electron microscope (Fig. 2.14). In principle, spherulites have a spherical shape, but as a result of the various crystallization conditions spherulites are sometimes fan-shaped or have other forms. Fibrils radiate out from the centre of a spherulite. Detailed structure investigations have shown that the polymeric chains are arranged in a spherulite tangentially or at least have a tendency to arrange themselves in this fashion. Spherulites grow upon crystallization in such a way that the axis "c" of the crystal coinciding with the direction of the chain axis is perpendicular to the spherulite radius in the fibril. As a result, the "b" axis of the polymer crystal is directed along this radius.

It is supposed (12) that the maximum growth of spherulites occurs in the "b" direction. The tangential arrangement of polymeric chains in spherulites agrees well with the concept of the folded chain conformation in crystals and the conditions under which polymer crys-

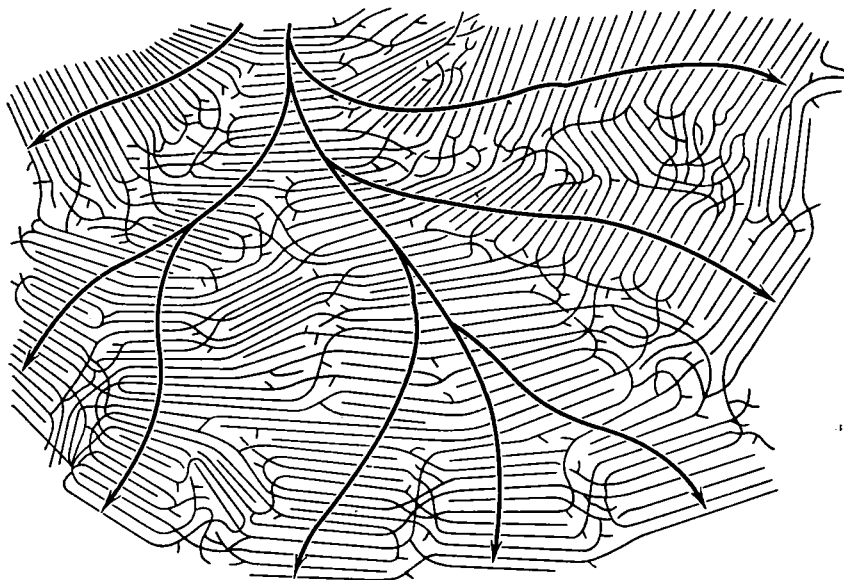


Fig. 2.15. Schematic representation of the arrangement of polyethylene macromolecules (after Bunn).

tals are growing. Figure 2.15 shows a schematic disposition of molecules in a polyethylene spherulite according to Bunn (12). From this figure it can be seen that the radial growth of crystals leads to the formation of spherulites.

A different viewpoint on the structure of spherulites has been advanced by Keller (16) and Morgan (17). They maintain that long fibrillar crystals extended in the "c" direction fold into helices. Groups of helices, which emerge from a single centre, produce spherulites. In order to account for the tangential disposition of the chains in a spherulite one has to presume that the helices are folded so tightly that the angle between the polymer chain and the helix axis exceeds 54° . The hypothesis of the tightly folded helices formed by fibrillar crystals has not, however, been reliably confirmed by experiment.

Fischer (18) believes that spherulites are formed by lamellar crystals, which periodically change their orientation and are twisted along the spherulite radius.

The question of the inner structure of spherulites remains to be controversial. Frenkel, for example, objects to using the term "fibril" for spherulites and believes that spherulites are formed by rays (19) that radiate from the centre. Based on detailed experimental investigations (20), which have shown that the rays have a complex supermolecular structure with alternating runs of crystallites and amorphous regions, Frenkel draws a substantial distinction between the ray and the fibril. The point is that in fibrils the *c* axis of crystallites

is parallel to the axis of the fibril itself, and in the ray this axis is at right angles to the spherulite radius, i.e., the ray axis. We shall consider fibrils in more detail at a later time, in the section devoted to the supermolecular structure of oriented polymers.

The term "ribbon" is often used in the literature in this country. By "ribbons" are usually meant extended aggregates composed of lamellae. Thus, lamellae are independent structural units from which there can be built more complex supermolecular structures, including spherulites.

The radial structure of spherulites is well disclosed by the methods of optical and electron microscopy. When thin sections or films of spherulite-containing polymers are observed under the optical microscope in the polarized light, dark crosses (Maltese crosses) are seen against the background of general luminescence. Such a picture is observed in studies of inorganic and low-molecular-mass substances. The appearance of dark crosses is accounted for by the presence of numerous crystals, which radiate out from a common centre and have a crystallographic axis directed along the radius from the centre. The arms of a dark cross are parallel to the direction of polarization and are formed by crystals in extinction positions. Crystals that have a different orientation seem to be illuminated.

It has been thought for a long time that the mechanical properties of polymers depend, to a considerable extent, on the spherulite size. Indeed, some of the parameters that characterize the mechanical properties of polymers (say, their strength) are sometimes considerably affected by the spherulite size. But it is very difficult to prove experimentally that there exists a unique relationship between the spherulite size and the mechanical properties of polymers, since a change in the spherulite size is usually accompanied by changes in the crystallinity, dimensions and degree of imperfection of the crystallites and in the state of the amorphous regions. Naturally, it is sometimes difficult to establish the effect of which of the above-mentioned factors is predominating. At least it seems unjustifiable to regard all the changes in the mechanical properties as resulting only from a change in the spherulite size.

The main morphological form in oriented polymers is the fibril (the microfibril). In supermolecular formations called fibrils the polymeric chains are preferentially oriented along the major fibril axis. A further important feature of the fibril is the existence in it of sufficiently distinct side boundaries. In oriented crystalline polymers the fibril has a complex structure and is composed of alternating crystalline and amorphous regions.

There are several models which account for the chain morphology in the microfibril. X-Ray diffraction studies lead to the conclusion that one of the types of supermolecular organization of chains that make up the microfibril is the coexistence of folded crystals and

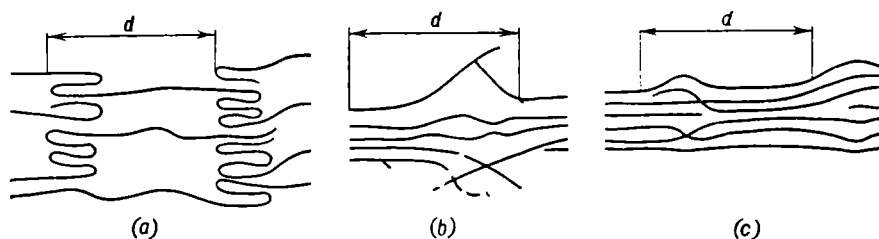


Fig. 2.16. Three models of a microfibril:

a—the Hosemann-Bonart model; *b*—the Hearle model; *c*—the Statton model.

disordered (amorphous) regions, which are crossed by a relatively small number of chains which connect the neighbouring crystals (Fig. 2.16). This model of the microfibril (the Hosemann-Bonart model) is most frequently resorted to for the explanation of a number of physical properties of oriented polymers.

The Hosemann-Bonart model is not the only one possible. There are other models of microfibrils in which there is no need to resort to the assumption of the existence of folded crystals. One such model is the fringed fibril model (the Hearle model) which is a further extension of the fringed micelle model. Figure 2.16 shows three possible models of the microfibril. By using direct structural methods of investigation it is impossible at present to prove experimentally the existence of this or that form of the supermolecular structure inside the microfibril and to make a choice among the available microfibril models. The Hosemann-Bonart model seems to be preferable at first glance (at least for oriented flexible-chain crystalline polymers) since it deals with one of the main structural units—the folded crystallite which is the simplest morphological form most frequently encountered in crystalline polymers (not only oriented polymers). But the intuitive approach to the selection of the possible microfibril model is not sufficiently convincing.

Of great importance for the understanding of the structure of crystalline polymers is the conception of the nature of the supermolecular structure of amorphous regions. The amorphous regions in a crystalline polymer may have various structures ranging from totally disordered portions (the network entanglement junctions, end groups, regions with disturbed stereoregularity) to portions exhibiting a certain order in the arrangement of chains and capable of being crystallized under favourable conditions.

The presence of regions, which are intermediate between the crystalline and the liquid state with respect to the degree of order, is characteristic of polymers.

One of the forms of such an intermediate state is paracrystalline regions. The concept of an ideal paracrystal has been introduced by Hosemann (21). A distinctive feature of the ideal paracrystal

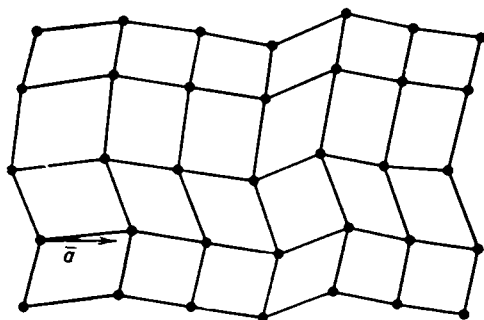


Fig. 2.17. The ideal paracrystal model.

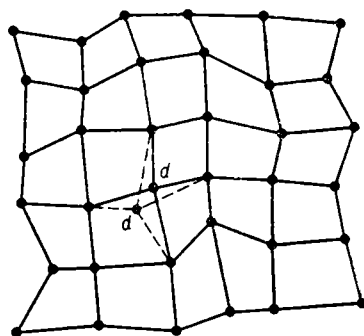


Fig. 2.18. Schematic representation of a two-dimensional paracrystal lattice.

(Figs. 2.17 and 2.18) is that all its unit cells are parallelepipeds. Therefore, the vectors that form any sequences in it (these may be, for example, sequences running upwards, from right to left, etc.), are equal and parallel to one another. If we use this model for the description of an assembly of closely spaced polymeric chains, all the chains will turn out to be equally deformed. They will be displaced in a vertical and a horizontal line parallel to one another. Thus, the paracrystal is one of the forms of disorder (Fig. 2.19).

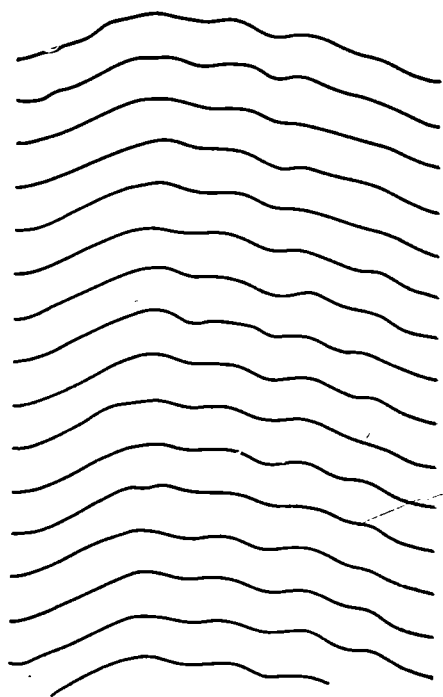


Fig. 2.19. Paracrystalline lattice layers

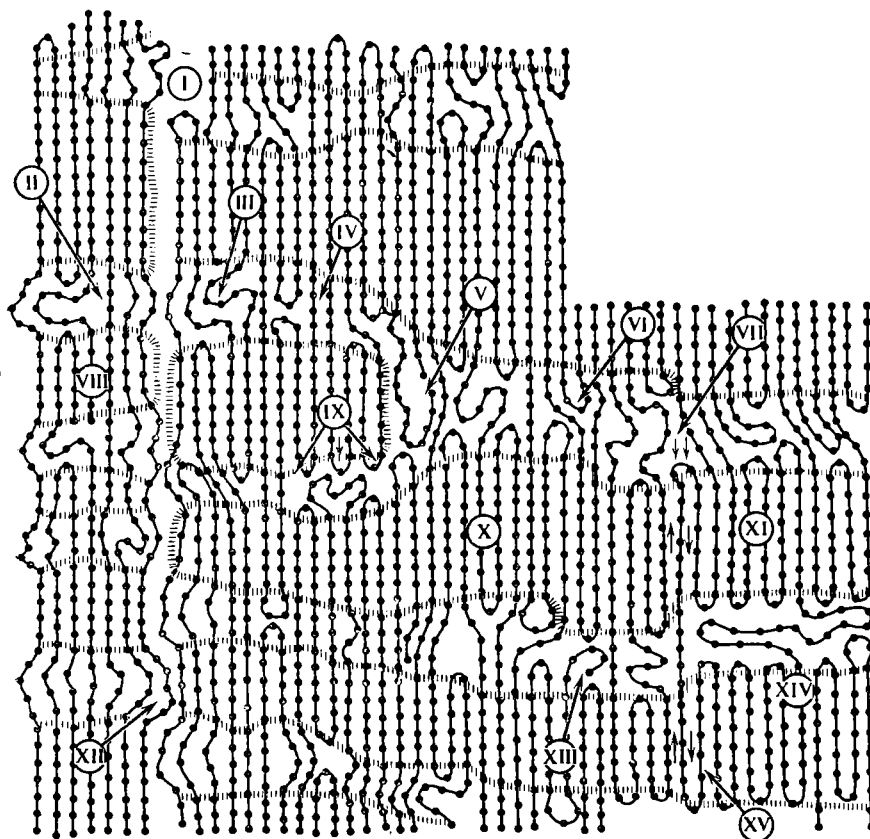


Fig. 2.20. The structural model for an oriented linear crystalline polymer (after Hosemann):

I—voids; II—the Statton model; III—the amorphous region; IV—straightened-out chains; V—crystals formed in block materials; VI—long folds (after Flory); VII—migrating folds; VIII—monofibrils formed on cold drawing; IX—short folds (after Keller); X—lattice formed by paracrystalline layers; XI—cluster consisting of fibrils formed on hot drawing; XII—fibrils corresponding to a four-point X-ray diagram; XIII—chain end; XIV—single crystals; XV—displacement region.

The most general form of paracrystalline disorder with a certain coordination number being retained is depicted in Fig. 2.18. It is evident that, in contrast to the ideal crystal, the sequences of vectors in such a system of points are not parallel to one another. Hence, the paracrystal is in a state which is intermediate between crystal and liquid with respect to the degree of order. Paracrystalline regions have been detected experimentally in a number of crystalline polymers (polyethylene, polyethylene oxide) (23).

Thus, crystalline polymers are characterized by a large variety of morphological forms. Figure 2.20 shows the Hosemann structural model of a linear crystalline polymer (23). The left part of the figure shows the model of a crystalline polymer subjected to cold drawing;

the right part shows the structure of an annealed block polymer; shown below on the right are single crystals.

The state of amorphous regions in a crystalline polymer differs from the state of a fully amorphous sample of the same polymer. Since one polymeric chain may run through crystallites and amorphous regions situated between these crystallites, it is natural that such chains in a partly crystalline polymer is usually in a somewhat stressed state. An increase in crystallinity leads, as a rule, to an increase in the mechanical stress that acts on the amorphous regions. On the other hand, the stressed units of polymeric chains that are part of the amorphous phase exert a mechanical effect on crystallites through which these chains pass. As a result, the crystallites are sometimes in a state of stress, which leads to a decrease in the melting temperature. At the same time, the orienting effect of crystallites on the chain units passing through amorphous regions may lead to an increase in the glass-transition temperature of the amorphous portion of the polymer. Thus, the state of crystalline regions depends to a certain extent on the state of amorphous regions and vice versa.

2.3. The Supramolecular Organization of Amorphous Polymers

It has long been thought that amorphous polymers are aggregates of randomly entangled molecules. The concept of molecular felt was developed, which was assumed to correspond to the structure of an amorphous polymer. As the well-known American scientist A. Tobolsky put it (24), "...the structure of an amorphous polymer may be likened to a bowl of cooked spaghetti; 'spaghetti-like' molecules are in constant random motion, the amplitude and velocity of which depend on temperature".

At the same time, on the basis of X-ray studies it may be concluded that in amorphous polymers (just as in ordinary liquids and other amorphous substances) there are regions of short-range order in which a single type of spatial orderliness is retained at a distance of 10-15 Å from any point. As far back as 1948 Alfrey (25) wrote that there must be ordered regions in amorphous polymers. But the question of the ordered arrangement of chains in amorphous polymers was first put forward by Kargin, Kitaigorodsky and Slonimsky (26). In 1957 these authors proposed a model for the structure of an amorphous polymer. According to this model, two types of supramolecular structure are possible in amorphous polymers.

Amorphous polymers may consist either of globules formed by folded polymer molecules or of extended chains which form bundles (an ordered bundle-like structure) (Fig. 2.21). It was supposed that the bundle length is much longer than the length of the macromole-

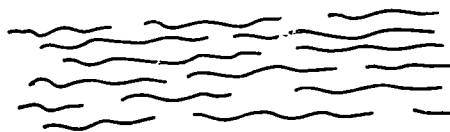


Fig. 2.24. The bundle model.

cules that make up the bundle. It was further assumed that bundles may display a certain flexibility and, as a result of this, there can occur the unfolding of the bundle regions, inside which the chains are twisted into helices, or the concerted rotations of one portion of the bundle relative to another about the C—C bonds. The concept of such cooperative rotations of chains within the bundle correlated well with the results of direct investigations of amorphous polymers by methods of optical and electron microscopy (27), which have shown that particles of some amorphous polymers, obtained by precipitation from solution, have a regular geometric form.

Kargin, Slonimsky, and Kitaigorodsky maintained that bundles exist not only in the glassy and rubbery states but also in the visco-fluid state. It was believed that bundles are analogous, to a certain extent, to regions of short-range order in liquids and that they are of a fluctuational nature. It was stressed that the lifetime of a bundle of polymeric chains is very long, and in the glassy state the bundle remains practically unchanged. Having advanced the bundle-like structure of an amorphous polymer, Kargin, Slonimsky, and Kitaigorodsky revised the concepts of chain morphology in crystalline polymers. In 1957 these authors stated (26): "The picture of the structure of a crystalline polymer widely adopted at present, in which it is visualized as a system of small ordered regions having common chains that run successively through regions of ordered and randomly entangled chain portions, cannot be valid in the form it is usually presented. This is clear even from pure geometric considerations: considering that the dimensions of ordered regions and the distances between these regions are sufficiently well known, it can be asserted that it is impossible to construct a polymer model in which the chains could leave the ordered regions, become entangled and then again form ordered regions. Undoubtedly, one chain runs through several ordered (crystalline) and disordered (amorphous) regions. But the chain does not go beyond the boundaries of the bundle and retains its neighbours along its entire length."

It is obvious that the above statement contradicts the present-day views on the structure of crystalline polymers and completely rejects the well-known Hosemann-Bonart model, which is used today by the majority of investigators.

The bundle model of the supermolecular structure of polymers has been further developed by Kitaigorodsky (28) who presumed that in the amorphous state in the direction of the chain axis there must

exist a certain orientation of chain units, while across the bundle there is only a short-order range with respect to both the distance between the axes and their orientation. Kitaigorodsky has introduced the concept of the "gas-crystalline state" in which the centres of monomeric units form a regular three-dimensional lattice and the azimuths of the molecules are randomly distributed in the bulk of the polymer. The special features of the gas-crystalline state are a long-range order in the arrangement of the molecular axes across the bundle and the absence of orientational order.

A number of factors are in favour of the bundle model: a small (about 10 per cent) difference in density between the crystalline and amorphous regions of the same polymer; a high rate of crystallization of some flexible-chain polymers (say, polyethylene). All these findings lead to the idea that ordered regions, which are "building blocks" for crystallites, must also be contained in a polymer in the amorphous state. Numerous attempts have been made to prove experimentally the existence of bundles in amorphous polymers. However, according to the opinion of the well-known American scientist P. H. Geil (14), who almost literally cites the article written by Kargin, Slonimsky and Kitaigorodsky (26), the microphotographs given as a proof of the bundle model cannot be regarded as being convincing. To prove the propositions advanced by Kargin, Slonimsky and Kitaigorodsky, one has to have more detailed microphotographs and electron diffraction patterns of globules and bundles.

The bundle model has been critically revised in recent years (22, 29, 30, 31). Vainshtein (22), while studying the diffraction of X-rays by an amorphous polymer, came to the conclusion that the structural model of such a polymer cannot be likened to the bundle-like structure. In his opinion, the length of portions where the polymer molecules are parallel to one another are not great and are approximately equal to their width. These portions gradually pass into one another and both inside them and in the transient zones there are formed "skew" contacts between the molecules. A stable bundle should have given a considerably larger number of distinct diffraction spots than are observed experimentally. Besides, the bundle-like structure does not agree (29) with the basic propositions of the kinetic theory of rubber elasticity, which is well confirmed by experiment. A different model of the supramolecular structure of amorphous polymers has been suggested by Yeh (32-34). Using the results of electron-microscopic investigations on a number of amorphous polymers, he came to the conclusion that the amorphous state of polymers is characterized by the presence of ordered regions (domains or "grains") formed by molecules that have a folded conformation. The domains are joined by chains that run through several crystalline and amorphous regions (Fig. 2.22). The interdomain regions consist of units of randomly arranged chains and also con-

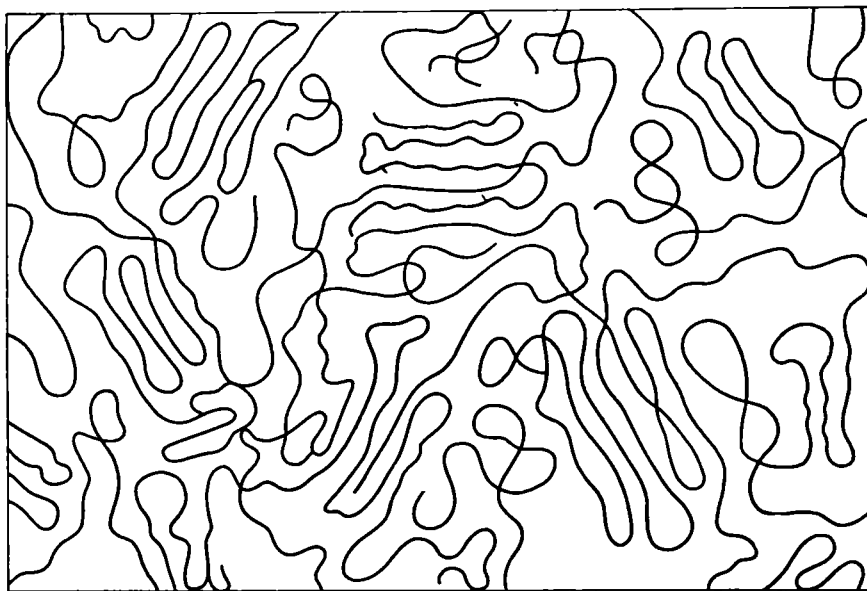


Fig. 2.22. The structural model of an amorphous polymer (after Yeh).

tain chains that participate in more than one crystallite, and free chain ends that have not become part of the domains. In essence, the model of the supermolecular organization of amorphous polymers proposed by Yeh is analogous to the Hosemann-Bonart structural model of crystalline polymers.

The idea put forward by Yeh has been further extended in the model proposed by Arzhakov, Bakeev and Kabanov (29). Unlike Yeh, who maintains that the primary structural unit is the domain, these authors believe that an amorphous polymer consists of closely packed fibrils. In this model, it is assumed that each fibril of an amorphous polymer is composed of folded domains connected through chains. The available experimental data (30), however, do not allow one to regard the fibril as the basic form of the supermolecular organization of an amorphous polymer.

There have been developed models (21, 23, 35) in which an amorphous polymer is considered to be a disordered crystal.

Robertson (31) gives a detailed analysis of the results of investigations into the supermolecular organization of polymers in the amorphous state carried out with the aid of density measurements, small-angle and wide-angle X-ray diffraction and neutron diffraction, electron microscopy, electron diffraction, thermoelasticity studies, strain birefringence, Rayleigh scattering, etc. Based on this analysis, Robertson came to the conclusion that in amorphous polymers there is localized regions of order, which leads to the retention of anisotropy over a distance of the order of several tens of angströms.

The results of small-angle X-ray scattering show that ordered regions have no distinct borderlines. According to Robertson, there is no experimental evidence for the presence in amorphous polymers of domains about 100 Å in size with regular equilibrium structures. In his opinion, domain structures that have been observed with the aid of electron microscopes and small-angle X-ray scattering can be attributed to the existence of contaminants or nonequilibrium structures.

The available experimental data evidently do not permit a unique description of the morphology of polymer chains in the amorphous state. The cluster model has been proposed to account for the supramolecular organization of amorphous polymers (36). By clusters we shall mean regions with molecules or their parts being more closely packed and/or with a more ordered arrangement of these as compared with the looser and disordered bulk of the substance. Naturally, the density of a cluster must somewhat exceed the average density of the polymer. At the same time, clusters are less ordered and less closely packed regions than crystallites.

There are clusters in which a more ordered arrangement of macromolecules can be achieved under certain conditions, i.e., clusters capable of crystallization (crystallizable or "crystalline" clusters). On the other hand, the existence of totally noncrystallizable ("anticrystalline") clusters is possible. Since no regular packing of polymeric chains in three dimensions is present in this case, it follows that when being cooled from melt the anticrystalline clusters cannot grow infinitely without voids or discontinuities being produced. It may be supposed that in polymers, alongside the crystalline regions there are also crystallizable and noncrystallizable clusters. In view of this, a polymer may be looked upon as an assembly of individual regions occupying different volume fractions $\varphi_1, \varphi_2, \varphi_3, \dots$ of the total volume of the polymer and being organized in different ways. From this viewpoint, an amorphous polymer may be regarded as an assembly of noncrystallizable (anticrystalline) clusters which are surrounded by less ordered and looser regions. A crude approximation of the cluster model is the concept of an amorphous polymer being depicted as a system consisting of anticrystalline clusters dispersed in an amorphous matrix. So the density of an amorphous polymer may be represented in the form

$$\rho = \varphi_1 \rho_1 + \varphi_2 \rho_2 = \varphi_1 \rho_1 + (1 - \varphi_1) \rho_2 \quad (2.22)$$

where ρ_1 and ρ_2 are the densities of anticrystalline clusters in the polymer and the density of the amorphous matrix, respectively; φ_1 and $\varphi_2 = 1 - \varphi_1$ are the volume fractions of clusters and amorphous matrix in the polymer, respectively.

Thus, it turns out that the density of an amorphous polymer is directly proportional to the volume fraction of clusters. It is therefore clear why the density of amorphous polymers increases when they are subjected to annealing. Evidently, the annealing of amorphous polymers leads to an increase in the number of anticrystalline clusters, to increased average dimensions of these formations and to a more ordered arrangement of polymeric chains in it. In order to determine, with the aid of formula (2.22), the volume concentration of clusters φ_1 in an amorphous polymer, it is necessary to know two parameters (ρ_1 and ρ_2) which are characteristic of each amorphous polymer. The density of the disordered matrix ρ_2 can be determined experimentally, but the determination of the density of clusters ρ_1 remains to be problematic. If we put, at a first approximation, $\rho_1 = \rho_{cr}$ (where ρ_{cr} is the density of crystallites), then φ_1 will be approximately equal to 0.6 for a number of amorphous polymers in the glassy state.

A specific feature of the cluster model is that the chain morphology inside a cluster is not specified. A cluster may consist either of macromolecules in the folded conformation (in which case the cluster model coincides with the Yeh model) or of extended units of polymeric chains which do not form (or form a small number of) folds. A second special feature of the cluster model is the assumption of the fluctuational nature of clusters. In the viscofluid and rubbery states the intensive segmental motion may lead to a strong reduction of the lifetime of clusters, to such an extent that they cease to exist. In a number of cases, the clusters evidently are simply destroyed by thermal motion. As the temperature is lowered the lifetime of clusters increases, and in the glassy state it becomes sufficiently long. In this state, clusters can exist for an infinitely long time.

The nature of chain morphology in clusters is probably determined by the structure of the polymer, its molecular mass and, to a considerable extent, by the parameters of the entanglement network (37). If the distance between two neighbouring entanglement junctions is sufficiently large and corresponds to the length of several tens (or more) of monomeric units (for example, in atactic polystyrene this distance is 45-60 monomeric units), then it is obvious that the most probable conformation inside the cluster is the folded chain conformation. Such a picture must probably be observed in many polymers with chains not too rigid. If the distance between two neighbouring entanglement junctions covers several repeating units, then it is obvious that the conformation corresponding to the extended chain will be the most probable one inside the cluster. Within the framework of this model it becomes clear that the maximum possible volume concentration of clusters φ_1 for a given amorphous polymer (just as the maximum degree of crystallinity α in a crystalline polymer) is specified by the entanglement network parameters.

The cluster model permits one to establish and trace out the intimate "genetic" relationship between the amorphous and crystalline states of polymers.

References

1. Kargin, V. A. and G. L. Slonimsky, *Brief Essays on the Physical Chemistry of Polymers*, 2nd ed., Khimiya, Moscow, 1967 (in Russian).
2. Keller, A., *Phil. Mag.*, **2**, 21, 1171 (1956).
3. Kitaigorodsky, A. I., *X-Ray Structure Analysis*, Gostekhizdat, Moscow, 1950 (in Russian).
4. Kitaigorodsky, A. I., *The X-Ray Structure Analysis of Finely Crystalline and Amorphous Bodies*, Gostekhizdat, Moscow, 1952 (in Russian).
5. Boky, G. B. and M. A. Porai-Koshits, *A Practical Course of X-Ray Diffraction Analysis*, Izd. MGU (Moscow University Press), Moscow, vol. 1, 1951; vol. 2, 1960 (in Russian).
6. Kheiker, D. M. and L. S. Zevin, *X-Ray Diffraction*, Fizmatgiz, Moscow, 1963 (in Russian).
7. Guinier, A., *Théorie et technique de la radiocristallographie*, Dunod, Paris, 1956.
8. Martynov, M. A. and K. A. Vylegzhanina, *The X-Ray Structure Analysis of Polymers*, Khimiya, Leningrad, 1972 (in Russian).
9. Hermans, P. H. and A. Weidinger, *Makromol. Chem.*, **44-46**, 24 (1961).
10. Weidinger, A. and P. H. Hermans, *Makromol. Chem.*, **50**, 98 (1961).
11. Ke, B. (editor), *Newer Methods of Polymer Characterization*, Wiley-Interscience, New York, 1964.
12. Bunn, C. W., in: *Polythene*, ed. by A. Renfrew and Ph. Morgan, London-New York, 1960.
13. Keller, A., in: *Fibre Structure*, ed. by J. W. S. Hearle and R. H. Peters, Butterworths, Manchester and London, 1963.
14. Geil, P. H., *Polymer Single Crystals*, Wiley, New York, 1963.
15. Mandelkern, L., *Crystallization of Flexible Polymer Molecules*, McGraw-Hill, New York, 1964.
16. Keller, A., *J. Polymer Sci.*, **17**, 355 (1955).
17. Morgan, L. B., *J. Appl. Chem.*, **4**, 160 (1954).
18. Fischer, E. W., *Discuss. Faraday Soc.*, **25**, 205 (1958).
19. Frenkel, S. Ya., in: P. H. Geil, *Polymer Single Crystals*, Khimiya, Moscow, 1968 (in Russian).
20. Marikhin, V. A., *The Author's Abstract to Candidate's Dissertation*, Fiz.-Tekhn. Inst. Akad. Nauk SSSR, Leningrad, 1966 (in Russian).
21. Hosemann, A., *Z. Phys.*, **128**, 4, 465 (1950).
22. Vainshtein, B. K., *Diffraction of X-Rays by Chain Molecules*, Elsevier, Amsterdam, 1966.
23. Hosemann, R., *J. Polymer Sci.*, **C**, **20**, 1 (1967).
24. Tobolsky, A., *Properties and Structure of Polymers*, Wiley, New York, 1960.
25. Alfrey, T., *Mechanical Behaviour of High Polymers*, Interscience, New York, 1948.
26. Kargin, V. A., A. I. Kitaigorodsky, and G. L. Slonimsky, *Koll. Zhurn.*, **19**, 2, 131 (1957).
27. Kargin, V. A., N. F. Bakeev, and Kh. Vergin, *Doklady Akad. Nauk SSSR*, **122**, 1, 97 (1958).
28. Kitaigorodsky, A. I., *Doklady Akad. Nauk SSSR*, **124**, 4, 861 (1959).
29. Arzhakov, S. A., N. F. Bakeev, and V. A. Kabanov, *Vysokomol. Soedin.*, **15**, 5, 1154 (1973).

30. Zaides, A. A., in: *Chemistry and Technology of High-Molecular-Mass Compounds* (Results of Science and Engineering), vol. 6, VINITI, Moscow, 1975 (in Russian).
31. Robertson, R. E., *Ann. Rev. Mater. Sci.*, **5**, 73 (1975).
32. Yeh, G. S., *J. Macromol. Sci.*, B, **6** (3), 465 (1972).
33. Yeh, G. S., *Pure Appl. Chem.*, **31**, 1, 65 (1972).
34. Brady, T. E. and G. S. Yeh, *J. Macromol. Sci.*, B, **7** (2), 243 (1973).
35. Pechhold, W. and S. Blasenbrey, *Angew. makromol. Chem.*, **22**, 306, 3 (1972).
36. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers, Moscow, 1975.
37. Perepechko, I. I. and O. V. Startsev, *Akust. Zhurn.*, **22**, 5, 749 (1976).

The Physical States of Polymers

3.1. The Concept of the Physical States

It is well known that substances can exist in three states of aggregation—gas, liquid, and solid. The aggregate states are determined by the nature of thermal motion of molecules or atoms that make up a substance. The most intensive thermal motion is characteristic of the gaseous state, the least intensive of the solid state. As a rule, the solid state is also characterized by the closest packing of atoms and molecules in a substance. The liquid state is intermediate between the gaseous and the solid state. We shall show at a later time that the concepts of the three states of matter are insufficient for the properties of polymers to be characterized. The concept of the phase state is not sufficient for this purpose either.

The thermodynamic definition of the phase is as follows. A phase is a part of a system, uniform throughout in chemical composition and physical properties, which is separated from other homogeneous parts of the system by boundary surfaces. There also exists a structural definition of a phase based on the difference in the degree of order in the arrangement of atoms or molecules.

The crystalline phase is characterized by three-dimensional long-range order in the arrangement of atoms or molecules that make up a substance.

Liquids are in a phase state which is typically devoid of a crystal lattice. This phase state is usually called the amorphous state. In the liquid phase there is no three-dimensional long-range order in the arrangement of molecules (or parts of molecules), but there is short-range order usually extending over not more than 10-15 Å from any chosen molecule. Evidently, these concepts are not sufficient for the description of the state of an amorphous polymer in the glassy state, say, atactic polystyrene at room temperature, this polymer being a typical amorphous polymer. On the one hand, such a polymer meets the criteria formulated for the solid state of matter; on the other hand, it can by no means be classified as a crystalline phase. Hence, while being a liquid by its physical state, such a polymer is in fact in the solid state of aggregation. Thus, the state of this polymer may be classified as the solid state in which, however, there is no three-dimensional long-range order.

From the foregoing it follows that such conceptions as the phase and physical states are insufficient for the characterization of polymers.

In this connection there has been introduced the concept of three physical states in which polymers can exist: the viscofluid state, the rubbery state and the glassy state. The *viscofluid state* of polymers is characterized by the possibility of the intensive thermal motion of individual units, large fragments of the polymeric chain (segments) and the movement of the macromolecule as a whole. This state is typical of most liquids. The most important specific feature of polymers existing in this state is the ability to flow under the influence of the applied stress (fluidity). The fluidity is characterized by viscosity, which as a physical phenomenon belongs to the class of transport processes and, like all transport processes, it is relaxational by its nature. The basic regularities that govern the viscosity of polymers and the viscofluid state are considered in detail in a number of review articles and monographs (1-5).

When the temperature is lowered, a liquid can crystallize or pass to the *glassy state*, which sets in when highly viscous liquids are overcooled. The transition to the glassy state is possible for both low-molecular-mass substances and polymers. In this state polymers are no longer capable of undergoing segmental motion. The glassy state is characterized by the vibrational motion; small units in the main chain and also atomic groups, which make up side pendant groups, can execute torsional vibrations. Low-molecular-mass liquids can pass directly to the glassy state when the temperature is lowered. However, polymers that have sufficiently high molecular masses pass, as a rule, from the viscofluid state first to the rubbery state.

The *rubbery (high-elastic) state* is characteristic of polymers only. In the rubbery state, individual units, atomic groups and segments undergo intensive thermal motion, but the movement of macromolecules as separate kinetic units is impossible. Polymers in the rubbery state possess remarkable mechanical properties. They are capable of undergoing enormous recoverable deformations, which sometimes amount to several hundred percent. The essence of this phenomenon consists in that the folded flexible long chains straighten out under the influence of the applied stress and return to their original shape after the stress is removed, as a result of thermal motion. The high-temperature limit of the rubbery state is the flow temperature T_f (above which the polymer is in the viscofluid state), and the low-temperature limit is the glass-transition temperature T_g (below which the polymer is in the glassy state).

3.2. The Rubbery State

The essence of the rubbery (high-elastic) state of polymers has been viewed from the standpoint of the molecular-kinetic theory and thermodynamics. The molecular-kinetic approach based on the laws of statistical physics allows one to explain most fully the relation-

ship between the macroscopic thermodynamic quantities and the behaviour of polymer molecules. The study of the rubbery state formerly involved the consideration of the presence of the various types of motion of flexible thread-like macromolecules. According to the kinetic (statistical) theory of rubber elasticity, a polymer is regarded not as an assembly of individual chains but rather as a sparse network which is composed of flexible constituent parts and which continuously changes its shape due to thermal motion.

3.2.1. The Elasticity of an Ideal Rubber.

The Kinetic Theory of Rubber Elasticity

Natural rubber is a typical polymer which is in the rubbery state at room temperature. Let us consider the basic regularities that characterize the deformation of natural rubber. Suppose that natural rubber consists of ideal macromolecules. The deformation of rubber is called high-elastic (rubber-like) deformation. The difference between rubbery and elastic deformation consists in the following.

1. The rubbery deformation is thousands and even tens of thousands of times greater than elastic deformation.

2. The mechanism of elastic deformation consists in an increase in the average distances between atoms and molecules, and in the case of polymers it reduces to a change in the bond lengths and to the deformation of valence angles. Elastic deformation is accompanied by a change in the volume of the body under the influence of the externally applied stress and its progress is associated with the change of the potential energy of the system. As a result of this, the solid body absorbs heat (cools down) on elastic extension and loses heat on compression. When amorphous polymers undergo rubber-like deformation, the volume of the sample does not change, as a rule. In many cases, rubbery deformation does not practically affect the potential energy of the system. When being stretched the specimen is heated and when it contracts it absorbs the same amount of heat.

3. Elastic deformation occurs with the velocity of sound and its rate is practically independent of temperature. The development of rubbery deformation is relaxational in character. Its rate increases very greatly on heating. The relaxation time may increase from tens and even hundreds of years (below T_g) to values of the order of 10^{-6} s at high temperatures.

The mechanism of high-elastic (rubbery) deformation has already been analysed (see Chapter 1). Recall only that the least probable form is the extended form of a long molecule since thermal motion disturbs the ordered arrangement of the chain. With a short relaxation time this leads to the bending and coiling of various parts of the macromolecule. The limiting case is the spherical form (a coil). This state, however, cannot be fully realized because of the restraints

imposed by the constancy of valence angles and of the hindered rotation about single bonds. By applying a tensile stress to the ends of such a chain it can be made to uncoil, which will result in its orientation. The decrease in entropy that takes place must be accompanied by the evolution of heat. After the stress is released a coil is formed again. In this process, as a result of thermal motion, the same amount of heat is absorbed.

The maximum amount of rubbery deformation of the chain is determined by its length h in the stretched state (the contour length) and by its dimensions in the coiled state. The first theory of rubbery deformation of polymers was advanced by Kuhn (6, 7).

3.2.1.1. *The Elasticity of a System of Isolated Polymeric Chains*

In Chapter 1 we derived expressions for the entropy, (1.7), and the elastic force, (1.13), of an isolated polymeric chain. Let us now establish the relationship between the deformation of individual molecules and of the sample as a whole (6-9). Let us consider, as a first approximation, the ideal model of a polymer. Suppose that the polymer in the rubbery state is regarded as an assembly of a large number of isolated chains which are not interconnected. Of course, such a model is a rather crude idealization of a real polymer. We assume that N is the number of chains in the sample, l_0 is the original length of the sample in the direction of the x axis, and A_0 is the cross-sectional area of the original sample. Further, suppose that the length and cross-sectional area of the stretched sample are, respectively, l and A . Assuming that the volume of the specimen does not change on extension, we may write: $l_0 A_0 = lA$. The elongation of the specimen is assumed to be small ($l \approx l_0$). Further, we shall assume that the relative deformation of each individual chain is equal to the relative deformation of the entire specimen. Proceeding from these assumptions, Kuhn, Mark, and Guth, and later Wall (8, 10, 11) found that the change in entropy of the sample that occurs as a result of extension is given by

$$S - S_0 = N \left[\frac{3}{2} - \left(\frac{\alpha^2}{2} + \frac{1}{\alpha} \right) \right] \quad (3.1)$$

where $\alpha = l_x/l_{0x} = h_x/h_{0x}$.

Using formula (1.12), we can obtain, from formula (3.1), the following expression for the tensile force:

$$f = \frac{NkT}{l_0} \left[\frac{l_x}{l_{0x}} - \left(\frac{l_{0x}}{l_x} \right)^2 \right] \quad (3.2)$$

The relationship between the stress σ and the deformation of an ideal rubber is obtained by dividing both parts of Eq. (3.2) by the

cross-sectional area A of the stretched specimen:

$$\sigma = \frac{f}{A} = nRT \left[\frac{l_x}{l_{0x}} - \left(\frac{l_{0x}}{l_x} \right)^2 \right] \quad (3.3)$$

where $n = N/(A_0 l_0 N_0)$ is the number of moles of rubber chains per unit volume; N_0 is Avogadro's number.

Utilizing formula (3.2), we can find the isothermal modulus of elasticity for any portion of the stress-strain relation:

$$E = l \left(\frac{\partial f}{\partial l} \right)_T \quad (3.4)$$

From Eqs. (3.2) and (3.4) it follows that

$$E = nRT \left[\frac{l_x}{l_{0x}} + 2 \left(\frac{l_{0x}}{l_x} \right)^2 \right] \quad (3.5)$$

Considering that at small deformations $l_x \approx l_{0x}$, we obtain:

$$E = 3nRT \quad (3.6)$$

With account taken of the relation $\rho = nM$ (where ρ is the density of natural rubber, and M is the mass of one mole of the chain) the expression for Young's modulus will assume the form

$$E = 3\rho RT/M \quad (3.7)$$

The main feature of the model considered is that the elastic properties of the isolated polymeric chains turn out to be due totally to thermal motion. By stretching rubber we perform work in order to overcome only the thermal motion, and the stretched elastomer contracts only because Brownian motion tends to disorientate the units of the extended macromolecules.

An immediate result of all the versions of the kinetic theory of rubber elasticity is the direct proportionality between the isothermal (equilibrium) elastic modulus and the absolute temperature. This relationship agrees well with experimental findings, and the values of the elastic modulus calculated from formula (3.7) coincide, by the order of magnitude, with the corresponding parameters of rubbers. It should be noted that the above-considered model is valid only for relatively small strains. It is interesting that this variant of statistical theory does not take into account the space network formed by the polymeric chains. Instead, it is tacitly assumed that there is no irreversible displacement of chains relative to one another on deformation.

More accurate calculations show that the quantity M in formula (3.7) is the upper limit of a certain integral. One of the founders of the kinetic theory of rubber elasticity, H. Mark, maintained, for example, that M characterizes the molecular mass of the "mobile part" of polymer molecules, thereby emphasizing that M in for-

mula (3.7) does not coincide with the molecular mass of the polymer determined by ordinary methods.

The theory of rubber elasticity was further developed by Mark, Guth, James, Flory, Treloar, Wall, Vol'kenshtein, Bartenev (4, 6-15, 28) and others, who took into account the fact that a real elastomer possesses a three-dimensional space network. In these theories, the model of an elastomer is a three-dimensional space network, the entanglement junctions of which are moving upon deformation.

3.2.1.2. *The Mechanical Behaviour of Network Polymers*

The classical theory of the deformation of the molecular network has been developed by Kuhn (6, 7). Below we shall consider this theory as modified by Treloar (16). Instead of the real space network formed by chemical cross-links, this variant deals with an idealized network which exhibits the following properties: (1) all the chains that form the network have the same length; (2) the entropy of the network is equal to the sum of the entropies of the individual chains; (3) the distribution of the chain end-to-end distances in the undeformed state is described by the Gaussian distribution function; (4) the volume is not changed upon deformation; (5) upon deformation the individual network chains distort in the same way as does the entire sample (the principle of affine deformation).

Note that the network chain is here taken to mean a part of the macromolecule located between two neighbouring entanglement points.

We shall confine ourselves to the consideration of a simple uniform extension. In view of the affine deformation of chains we shall consider the deformation of a single chain. Let one of its ends P is at the coordinate origin (Fig. 3.1) and the second at the point $Q(x, y, z)$. The chain end-to-end distance is defined by the coordinates x, y, z of the point Q . Suppose that upon deformation the chain end is displaced from the point $Q(x, y, z)$ to the point $Q'(x', y', z')$. The new coordinates x', y', z' of the point Q' are connected with the coordinates x, y, z of the point Q by the following relations:

$$x' = \lambda_1 x; \quad y' = \lambda_2 y; \quad z' = \lambda_3 z \quad (3.8)$$

where $\lambda_1, \lambda_2, \lambda_3$ are the extension ratios in three mutually perpendicular directions.

The coordinate axes are here chosen so that they coincide with the directions of the principal strains. Since the volume of the polymer remains unchanged upon deformation, it follows that $\lambda_1, \lambda_2, \lambda_3 = 1$. It should be noted that in the case of simple uniaxial extension the draw ratio $\lambda = \lambda_1$ and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$.

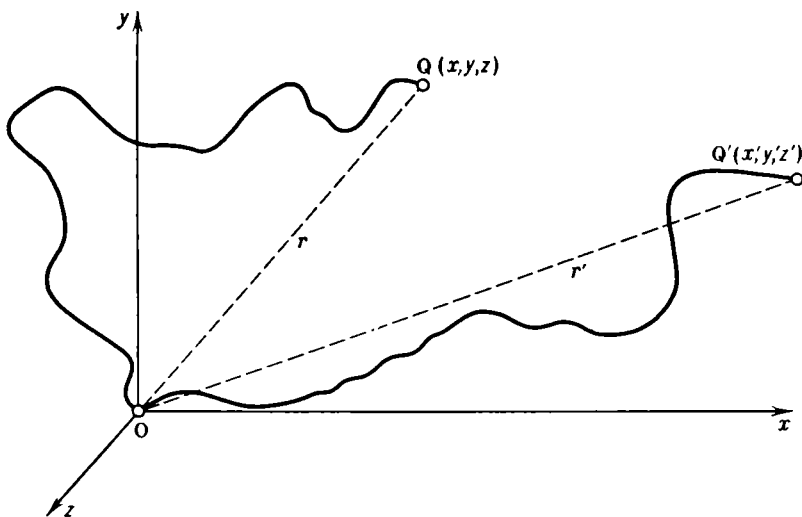


Fig. 3.1. The affine deformation of chains.

In accordance with the assumptions made, the entropy of the unit volume of the undeformed network is given by

$$S_0 = \int s_0 dN \quad (3.9)$$

where s_0 is the entropy of an individual chain in the undeformed state; dN is the number of chains in the undeformed state with its ends being in the volume element $dx dy dz$.

The quantity dN is given by the relation

$$dN = N \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2+y^2+z^2)} dx dy dz \quad (3.10)$$

where $\beta^2 = 3/(2zb^2)$; z is the number of repeating units; b is the length of one unit.

In accordance with formula (1.7), the entropy of an individual chain is given by

$$s_0 = C - \frac{3k}{2zb^2} (x^2 + y^2 + z^2) = C - k\beta^2 (x^2 + y^2 + z^2) \quad (3.11)$$

The total entropy of the unit volume of the unstrained network is

$$\begin{aligned} S_0 &= \\ &= \int s_0 dN = \frac{N\beta^3}{\pi^{3/2}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [C - k\beta^2 (x^2 + y^2 + z^2)] e^{-\beta^2(x^2+y^2+z^2)} dx dy dz \end{aligned} \quad (3.12)$$

The integral in expression (3.12) is evaluated in a fairly simple way:

$$\int_{-\infty}^{+\infty} e^{-\beta^2 x^2} dx = \frac{\sqrt{\pi}}{\beta}; \quad \int_{-\infty}^{+\infty} x^2 e^{-\beta^2 x^2} dx = \frac{\sqrt{\pi}}{2\beta^3};$$

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} x^2 e^{-\beta^2(x^2+y^2+z^2)} dx dy dz = \frac{\pi^{3/2}}{2\beta^5}$$

Utilizing these values of the integrals, it is not difficult to show that

$$S_0 = N \left(C - \frac{3}{2} k \right) \quad (3.13)$$

The entropy of each of the deformed chains is given, in accordance with formula (3.11), by the relation

$$s = C - k\beta^2 (\lambda_1^2 x^2 + \lambda_2^2 y^2 + \lambda_3^2 z^2) \quad (3.14)$$

The entropy of the unit volume of the deformed network is expressed by the following relation:

$$S = \int s dN = \frac{N\beta^3}{\pi^{3/2}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [C - k\beta^2 (\lambda_1^2 x^2 + \lambda_2^2 y^2 + \lambda_3^2 z^2)] e^{-\beta^2(x^2+y^2+z^2)} dx dy dz = N \left[C - \frac{1}{2} k (\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \right] \quad (3.15)$$

The entropy change resulting from the deformation will be equal to

$$S - S_0 = \frac{1}{2} Nk (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (3.16)$$

Assuming that the internal energy is not changed upon deformation, we find the free energy change:

$$\Delta F = -T\Delta S = \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (3.17)$$

Since it is assumed that the deformation is an equilibrium isothermal process, it evidently follows that the work in this case is numerically equal to ΔF . This allows one to establish the relationship between the stress and the rubbery strain. In the case of simple uniaxial extension in the direction of the axis x ($\lambda_1 = \lambda$; $\lambda_2 = \lambda_3 = \lambda^{-1/2}$) we obtain the following expression for the stress:

$$\sigma = NkT (\lambda^2 - \lambda^{-1}) \quad (3.18)$$

From Eq. (3.18) it follows that in the case of small deformations ($\lambda \approx 1$) the equilibrium elastic modulus is equal to:

$$E = \lambda \left(\frac{\partial \sigma}{\partial \lambda} \right)_{\lambda=1} = 3NkT \quad (3.19)$$

where N is the number of network chains in the unit volume.

The equilibrium elastic modulus may be represented in the form

$$E = \frac{3N}{N_0} RT = 3NkT = 3nRT = \frac{3\rho RT}{M_c} \quad (3.20)$$

where N_0 is Avogadro's number; R is the universal gas constant; $n = N/N_0$ is the number of moles of network chains per unit volume (the degree of cross-linking); M_c is the molecular mass of one mole of the network chain, i.e., the mass of one mole of the portion of the polymeric chain between two neighbouring entanglement points.

Thus, the kinetic theory of rubber elasticity leads to an interesting result of practical importance: the equilibrium elastic modulus is directly proportional to the degree of cross-linking (or inversely proportional to M_c).

At small deformations $\lambda \approx 1$ (considering that $\lambda = 1 + \epsilon$, where ϵ is the relative deformation). In this case, from Eq. (3.18) we obtain:

$$\sigma = E\epsilon \quad (3.21)$$

This formula is analogous to Hooke's law for solids. Equation (3.18) applies to both uniaxial compression and extension. Wall carried out an analogous calculation for the case of shear and came to the conclusion that the deformation of elastomers obeys Hooke's law even if this law is not satisfied on extension. Wall obtained a value for the shear modulus equal to NkT , as might be expected from the theory of elasticity if one takes into account that the Young modulus is equal to $3NkT$ and that the polymer is incompressible.

3.2.1.3. The James-Guth Theory

The most refined variant of the network theory of rubber elasticity has been worked out by James and Guth (14, 15). It is free from many of the drawbacks inherent in the Kuhn theory considered above.

One of the weakest points of the Kuhn theory is that it is based on the assumption that the network junctions are somewhat fixed (the displacement movement of the system is limited by the lengths of the chains between entanglement points).

James and Guth (14, 15) regard the network as a system of chains connected at the points of attachment. In their theory, it is assumed that the network junctions can themselves take part in the Brownian motion of the chains. It is only the position of the chains situated on the external surfaces of the sample that is specified. All the other network junctions are given a complete statistical freedom. The task reduces to calculating the total number of conformations of all the chains on condition that the fixed junctions lie in certain definite planes, and all the other junctions can occupy any possible position. It is assumed that the fluctuations in the position of each junction

of a network of Gaussian chains can be described by the Gaussian distribution function and the average force that acts between two neighbouring junctions is such as it would be if the junctions were fixed in their most probable positions.

Let us consider (14-17, 28) a sample of a rubber-like polymer, which has the form of a cube of the following volume before it is stretched:

$$V_0 = L_{0x}L_{0y}L_{0z} = L_0^3 \quad (3.22)$$

Suppose that after uniaxial extension the cube is transformed to a parallelepiped, the volume and linear dimensions of which are connected by the formula

$$V = L_x L_y L_z \quad (3.23)$$

We assume that the extension occurs under the influence of a force f directed along the z axis. Let us find the relationship between the stress and the strain.

It is obvious that the free energy of the rubber specimen can be represented in the following form:

$$F = E - TS \quad (3.24)$$

From this it follows that

$$dF = dE - T dS - S dT \quad (3.25)$$

The first law of thermodynamics may be written as follows:

$$dQ = dE + dA \quad (3.26)$$

where dQ is the small amount of heat supplied to the system; dE is an infinitesimal change in internal energy of the system; dA is the elementary work performed by the system against the external forces.

If the rubber sample is acted on by an external force \bar{f} , then the work done by this force along the path dL will be given by

$$\sum_{i=x,y,z} f_i dL_i$$

The work done by the system, i.e., the work performed by the internal (elastic) forces in the sample, against external forces will be equal to

$$\sum_{i=x,y,z} f_i dL_i$$

If we also take into account the work done against the pressure of the surroundings, the elementary work of the rubber sample can be represented in the form:

$$dA = P dV - \sum_{i=x,y,z} f_i dL_i \quad (3.27)$$

Considering that for reversible processes $dQ = T dS$, expression (3.26) may be written thus

$$dE = T dS - P dV + \sum_{i=x, y, z} f_i dL_i \quad (3.28)$$

Since

$$dV = L_x L_y dL_z + L_x L_z dL_y + L_y L_z dL_x \quad (3.29)$$

it follows that

$$dE = T dS + (f_x - PL_y L_z) dL_x + (f_y - PL_x L_z) dL_y + (f_z - PL_x L_y) dL_z \quad (3.30)$$

Substituting expression (3.30) into formula (3.25), we obtain:

$$dF = -S dT + \sum_{i \neq j \neq k} (f_i - PL_j L_k) dL_i \quad (3.31)$$

Since we are concerned here with extension along the z axis, it follows that $f_x = f_y = 0$ and $f_z = f$. From Eqs. (3.31) and (3.24) it follows that

$$\begin{aligned} -PL_y L_z &= \left(\frac{\partial F}{\partial L_x} \right)_{T, L_y, L_z} = \left(\frac{\partial E}{\partial L_x} \right)_{T, L_y, L_z} - T \left(\frac{\partial S}{\partial L_x} \right)_{T, L_y, L_z} \\ -PL_x L_z &= \left(\frac{\partial F}{\partial L_y} \right)_{T, L_x, L_z} = \left(\frac{\partial E}{\partial L_y} \right)_{T, L_x, L_z} - T \left(\frac{\partial S}{\partial L_y} \right)_{T, L_x, L_z} \end{aligned} \quad (3.32)$$

$$f - PL_x L_y = \left(\frac{\partial F}{\partial L_z} \right)_{T, L_x, L_y} = \left(\frac{\partial E}{\partial L_z} \right)_{T, L_x, L_y} - T \left(\frac{\partial S}{\partial L_z} \right)_{T, L_x, L_y}$$

From the first and third equations in (3.32) we obtain:

$$\begin{aligned} f &= \left(\frac{\partial E}{\partial L_z} \right)_{T, L_x, L_y} - \frac{L_x}{L_z} \left(\frac{\partial E}{\partial L_x} \right)_{T, L_y, L_z} - \\ &\quad - T \left[\left(\frac{\partial S}{\partial L_z} \right)_{T, L_x, L_y} - \frac{L_x}{L_z} \left(\frac{\partial S}{\partial L_x} \right)_{T, L_y, L_z} \right] \end{aligned} \quad (3.33)$$

Thus, the force f depends on a number of thermodynamic quantities that characterize natural rubber. On the other hand, the relationship between the thermodynamic quantities and the molecular structure is described by statistical mechanics. The thermodynamic functions of the system are determined with the aid of the statistical sum of states (the partition function)

$$Q = \sum_i g_i e^{-E_i/kT} \quad (3.34)$$

where E_i is the energy of the i th energy level of the system; g_i is the corresponding statistical weight which shows the number of system states, whose energies are equal to E_i [the statistical weight of the i th rotational isomer is determined by expression (1.17)].

If the partition function Q is known, we can readily find the main thermodynamic quantities. For example, the Helmholtz free energy per molecule is given by

$$F = -kT \ln Q \quad (3.35)$$

The internal energy and entropy are found in the following way:

$$E = kT^2 \frac{\partial \ln Q}{\partial T} \quad (3.36)$$

$$S = kT \frac{\partial \ln Q}{\partial T} + k \ln Q \quad (3.37)$$

Equations (3.35) through (3.37) establish a direct relationship between the thermodynamic functions and the parameters that are used in molecular theory. Thus, our task boils down to finding the partition function Q .

The partition function for a rubber-like specimen may be represented in the form

$$Q = Q_1(V, T) Q_2(L_x, L_y, L_z, T) \quad (3.38)$$

where Q_1 is the isotropic part which depends on L_x, L_y, L_z only through the volume; Q_2 is the anisotropic part which depends on the amount of extension.

For the internal energy and entropy we have, accordingly,

$$E = E_1(V, T) + E_2(L_x, L_y, L_z, T) \quad (3.39)$$

$$S = S_1(V, T) + S_2(L_x, L_y, L_z, T)$$

An analogous expression is obtained for the free energy:

$$F = F_1(V, T) + F_2(L_x, L_y, L_z, T) \quad (3.40)$$

From the first equation in (3.39) it follows that

$$\begin{aligned} \left(\frac{\partial E}{\partial L_z} \right)_{T, L_x, L_y} &= \left(\frac{\partial E_1}{\partial V} \right)_T \left(\frac{\partial V}{\partial L_z} \right)_{T, L_x, L_y} + \left(\frac{\partial E_2}{\partial L_z} \right)_{T, L_x, L_y} = \\ &= \left(\frac{\partial E_1}{\partial V} \right)_T L_x L_y + \left(\frac{\partial E_2}{\partial L_z} \right)_{T, L_x, L_y} \end{aligned} \quad (3.41)$$

Analogously, we obtain:

$$\left(\frac{\partial E}{\partial L_x} \right)_{T, L_y, L_z} = \left(\frac{\partial E_1}{\partial V} \right)_T L_y L_z + \left(\frac{\partial E_2}{\partial L_x} \right)_{T, L_y, L_z} \quad (3.42)$$

Substituting Eqs. (3.41) and (3.42) and the analogous expressions for the entropy into Eq. (3.33) yield:

$$f = \left(\frac{\partial F_2}{\partial L_z} \right)_{T, L_x, L_y} - \frac{L_x}{L_z} \left(\frac{\partial F_2}{\partial L_x} \right)_{T, L_y, L_z} \dots \quad (3.43)$$

In order to find the force f it is necessary to calculate the configurational partition function Q_2 , which is connected with the free energy F_2

by the following relation:

$$F_2 = -kT \ln Q_2 (L_x, L_y, L_z, T) \quad (3.44)$$

If we limit ourselves to a consideration of freely rotating chains ($E_2 = 0$), then $F_2 = -TS_2$.

In order to evaluate Q_2 , we have to find the number of chain conformations corresponding to the specified positions of the fixed points and a set of internal network points. Appropriate computations lead to the following relation:

$$Q_2 = K_1 \exp \left[-\frac{K}{2L_0^2} \left(L^2 + \frac{V}{L} \right) \right] \quad (3.45)$$

Here K_1 is a certain constant, and K is found from the formula

$$K = \frac{1}{b^2} \sum_{\tau > \nu} \sum (\bar{r}_{\tau\nu}^{(0)})^2 / z_{\tau\nu} \quad (3.46)$$

where $\bar{r}_{\tau\nu}^{(0)}$ is the vector connecting the mean positions of the τ th and ν th internal or fixed points in the unstretched specimen; b is the effective length of the link; $z_{\tau\nu}$ is the number of links in the chain.

The constant K calculated on the assumption that the vulcanization of rubber involves an instantaneous cross-linking of its chains is given by (10):

$$K = N \quad (3.47)$$

where N is the total number of chains in the sample.

Let us now find the retractive elastic force in the sample which compensates for the external stretching force. Using the relations obtained, we can write Eq. (3.43) in the following form:

$$f = \frac{KkT}{L_0^2} \left(L_z - \frac{V}{L_z^2} \right) \quad (3.48)$$

Introducing the relative deformations $\lambda_z = L_z/L_0$, $\lambda_x = \lambda_y = L_x/L_0$ and considering that $\lambda_x \lambda_y \lambda_z = \lambda_x^2 \lambda_z = V/V_0 = \omega$, we obtain:

$$f = \frac{KkT}{L_0} \left(\lambda_z - \frac{\omega}{\lambda_z^2} \right) \quad (3.49)$$

The force per unit cross-sectional area of the stretched sample (the true stress) is given by

$$\sigma = \frac{f}{L_x^2} = \frac{KkT}{\omega V_0} \left(\lambda_z^2 - \frac{\omega}{\lambda_z} \right) \quad (3.50)$$

The force acting on unit cross-sectional area of the unstretched sample (the conditional stress) is equal, in accordance with expressions

(3.48) and (3.49), to

$$\sigma' = \frac{f}{L_0^2} = \frac{KkT}{V_0} \left(\lambda - \frac{\omega}{\lambda^2} \right) \dots \quad (3.51)$$

from which we find the elastic modulus of the specimen at small deformations:

$$E = \left(\frac{\partial \sigma'}{\partial \lambda_z} \right)_{\lambda=1} = \frac{KkT}{V_0} (1 + 2\omega) \quad (3.52)$$

Rubbers (like linear amorphous polymers in the rubbery state) exhibit low compressibility and, because of this, their Poisson's ratio is close to 0.5. This means that the volume of natural rubber remains practically unchanged on deformation, i.e., $V = V_0$ and $\omega = 1$. Substituting these values into formula (3.52) and taking into account that $K = N$, we obtain the following relation for the elastic modulus of a specimen having the form of a cube whose volume is equal to unity:

$$E = 3N_1kT = 3\rho RT/M_c \quad (3.53)$$

One of the most significant results of the kinetic theory of rubber elasticity is the above-given relation between the equilibrium elastic modulus upon rubbery deformation and the degree of cross-linking.

The validity of the above-considered theory of rubber elasticity has been confirmed by numerous experiments. A comparison of the results of the kinetic theory of rubber elasticity of polymer chains and networks shows that the elastic moduli for chains and networks are defined by identical expressions. In this connection, there has been developed the conception that linear amorphous polymers in the rubbery state have a space network formed by chain entanglements rather than by chemical bonds. The existence of a spatial entanglement network in linear amorphous polymers leads to the manifestation of an equilibrium rubbery deformation in the rubbery state (at not too high stresses and temperatures). This analogy in the viscoelastic behaviour of cross-linked (network) and linear polymers is especially pronounced when the duration of the experiment is not too long, since otherwise there arises a difference caused by the slippage of the entanglement junctions in the networks formed by entanglements, whereas in ordinary networks no slippage occurs.

An important characteristic of the entanglement network is the parameter M_c , which is the molecular mass of the chain length between two neighbouring entanglement points. The concept of the existence of a spatial entanglement network in linear amorphous polymers is extensively used in the literature (17-20). Information on the parameter M_c for a number of polymers is given in the review article by Porter and Johnson (20).

The above-considered variants of the kinetic theory of rubber elasticity agree well with experimental data only in the region of small deformations. At large deformations there is observed a considerable discrepancy. This discrepancy arises because of the initial propositions and assumptions of the kinetic theory. Indeed, this theory does not take account of the contribution made by the change in the internal energy to the elastic force, which contradicts a number of experimental facts observed with large deformations. The use of the Gaussian distribution must also leads to a discrepancy between theory and experiment at large deformations. A special feature (and, possibly, a shortcoming) of the kinetic theory of rubber elasticity is that it does not take account of the intermolecular interaction, which does exist in the rubbery state, though it is not strong. Nevertheless, the kinetic theory of rubber elasticity has proved very successful in describing and explaining a number of physical (including mechanical) properties of polymers and in establishing the relationship between the three-dimensional structure and the physical properties of rubber-like polymers. This theory is one of the most thoroughly developed branches of polymer physics.

3.3. The Glassy State

3.3.1. Transition of Polymers from the Rubbery to the Glassy State

From the viewpoint of physical kinetics, the glassy state may be treated as a state in which the segmental mobility is "frozen". If the polymer in the rubbery state is gradually cooled, its viscosity increases and the intensity of molecular motion caused by the diffusion of the segments is decreased. Obviously, to each of the temperatures there will correspond a new equilibrium state, which is characterized by a certain structure even for amorphous polymers. Probably in each equilibrium state there is a certain definite chain end-to-end distance. This conclusion follows at least from the theory of glass transition worked out by Gibbs and DiMarzio (21), which will be considered later.

If the temperature of the polymer in the rubbery state is lowered, the equilibrium state corresponding to a new temperature will be attained only after a certain period of time. This time period is required for the kinetic units of the polymeric chains to be rearranged so that they occupy new positions corresponding to an equilibrium state at a new temperature. Thus, the transition from the rubbery state to the glassy state may be regarded as a series of relaxation processes; some of these processes have no chance to be accomplished. The latter circumstance applies mostly to the temperatures $T \leq T_g$.

The transition of the polymer from the rubbery to the glassy state is relaxational by its nature.

If the system is brought out of the equilibrium state under the influence of external forces (deformation, a change in temperature, etc.) and left to its own devices, it will reach a state of thermodynamic equilibrium under the effect of internal forces after a certain period of time. The process of transition of the system to a thermodynamic equilibrium state is called relaxation. The time during which any of the physical quantities, which is a measure of the departure of the system from the equilibrium state, decreases by e times is called the relaxation time. With a certain decrease in the temperature of the polymer an equilibrium state (a new equilibrium structure) corresponding to a new temperature will be attained only after the lapse of some time τ , which may be treated, at a first approximation, as the structural relaxation time. As the temperature is lowered the relaxation time τ will increase (approximately by an exponential law) and at a sufficiently low temperature it will become so long that the equilibrium state of the polymer and the corresponding structure will practically never be achieved. This state is what we call the glassy state.

Thus, the glassy state is a state of relative equilibrium, i.e., a metastable state (22). A specific feature of this state is that the polymer may exist in the glassy state for an infinitely long time. Such a prolonged existence of polymers in the state of relative equilibrium is probably due to the presence in them of sufficiently stable supermolecular structures.

The glassy state may be also treated as a solid state devoid of any crystalline structure. There is a different, alternative definition of the glassy state: it is sometimes regarded as a state typical of strongly thickened overcooled liquids.

The transition from the rubbery to the glassy state (just as the reverse process) usually occurs within a certain temperature range. It is sometimes stressed that this is one of the differences between the glass transition and a phase transition (say, melting or fusion). In fact, in the case of polymers this comparison is not sufficiently convincing since the melting of crystalline polymers occurs, as a rule, not at a point but within a range of temperatures from several degrees to several tens of degrees. The transition of polymers from the rubbery to the glassy state and the reverse process also occur within such a temperature range. For example, the temperature range (the width of the transient zone) within which glass transition takes place is 19°C for polycarbonates and 11°C for polysulphones.

For a number of polymers the transition from the rubbery to the glassy state occurs within a very narrow temperature range (10–20°C) as compared with the melting range of some crystalline polymers, which indicates that the glass transition is a highly cooperative

process. This cooperativeness of the process is in its turn due to the specific morphology of polymeric chains. It has been shown (23) that the high degree of cooperativity of segmental motion during the glass transition and, hence, the small width of the transient zone must be observed when the anticrystalline clusters in an amorphous polymer are formed by straightened-out portions of the chains that do not produce folds.

Nonetheless, the highly cooperative molecular motion, which is observed in a number of polymers upon glass transition, does not at all mean that the glass transition may be regarded as a thermodynamic phase transition. Numerous investigations have shown that the glass transition is not a phase transition and that it is a relaxational-type temperature transition. From the standpoint of the relaxation theory the transition to the glassy state may be looked upon as a relaxation process that cannot be brought to an end as a result of a very strong increase in the viscosity of the system and the associated sharp increase in the relaxation time with decreasing temperature. Thus, in the glassy state the structure, which is more or less close to an equilibrium structure at a temperature higher than the glass transition temperature T_g , is found to have been "frozen". It should be noted that from the viewpoint of relaxation theory the glassy state of polymers is a state in which the condition $\omega\tau_j \gg 1$ (where ω is the frequency of the periodic action on the polymer and τ is the relaxation time) is fulfilled for all τ_j associated with the segmental mobility of the main chains of macromolecules.

The physical properties of polymers in the glassy state differ very significantly from those in the rubbery state. The conditional borderline between these states is the glass-transition temperature. The glass temperature is the most important characteristic of amorphous polymers. The concept of the glass-transition temperature was introduced by Ueberreiter. Various attempts have been made to define the concept of the glass-transition temperature. Two definitions of T_g are most frequently used.

According to Staverman (24), the glass-transition temperature is the temperature at which the viscosity of the polymer is 10^{12} Pa·s. On the other hand, the glass temperature is defined as the temperature below which the segmental motion of polymer molecules is frozen. The latter definition may be formulated in a different manner. It may be assumed that T_g is the temperature above which the segmental motion in an amorphous polymer begins to be unfrozen.

There exist many experimental methods (5) of determining the glass temperature. The most reliable method is the determination of T_g from a change of slope in the temperature dependence of the specific volume on the condition that the sample under study is thermostatted for a sufficiently long time at each temperature point at which the measurements are made. This method of determination

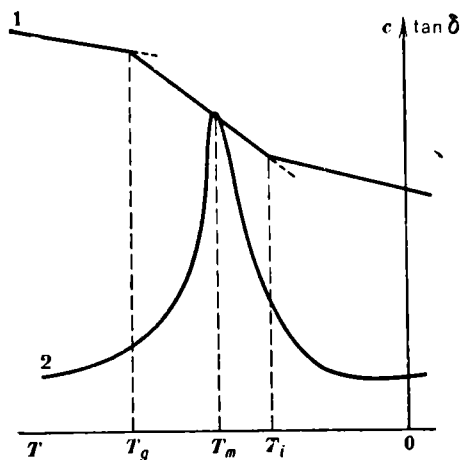


Fig. 3.2. The sound velocity c (1) and the loss factor (loss tangent) $\tan \delta$ (2) versus temperature for polytetrafluoroethylene near T_g (T_m is the temperature of the loss tangent peak; T_i is the high-temperature limit of the relaxation process).

of T_g is based on the fact that above T_g the thermal cubic expansion coefficient sharply increases, a circumstance responsible for the change of slope in the temperature dependence of the specific volume.

Acoustic methods have been used in recent years for the determination of the glass-transition temperature (19). In this case, the measured values of T_g may depend on the frequency of acoustic vibrations (in the dilatometric method of determination T_g may depend on the rate of heating or cooling), and what is measured is in fact the temperature of "mechanical" glass transition (4). When acoustic methods are employed, the glass temperature is determined from a change in the temperature coefficient of the sound velocity. In the glassy state, with the molecular mobility remaining unchanged the sound velocity depends linearly on the temperature. Above T_g , when the segmental motion of the micro-Brownian type begins to be unfrozen, the temperature coefficient of sound velocity undergoes a sharp change. The point on the temperature scale at which there is observed a very sharp change of slope in the temperature dependence of sound velocity (Fig. 3.2) is taken as the glass-transition temperature.

Such a method of determining T_g agrees well with the definitions of the glass temperature given above. Indeed, the glassy state is characterized by the condition $\omega\tau_j \gg 1$, to which there corresponds a linear dependence of the sound velocity on the temperature, the temperature coefficient of sound velocity being relatively small below T_g . The temperature at which the above condition is no longer satisfied is exactly the glass-transition temperature T_g ; above this temperature the segmental motion begins to be unfrozen, which leads to a sharp change in the temperature coefficient of sound velocity. Thus, at T_g there must be fulfilled the condition $\omega\tau_j = N$ for all τ_j associated with the segmental mobility of the polymer chains. Naturally, $N > 1$.

It is not difficult to show that this follows from the definition of T_g as the temperature at which the viscosity of the polymer assumes a value equal to 10^{12} Pa·s. Indeed, since the shear viscosity of the polymer may be represented in the form $\eta = G\tau$ (where G is the shear modulus and τ is the relaxation time), it follows that the relaxation time due to the segmental motion is equal to $\tau = \eta/G$. Since T_g is, by definition, the borderline point of the glassy state, it follows that at T_g the quantity $\eta = 10^{12}$ Pa·s and $G \approx 10^9$ dynes/cm² (at T_g the shear modulus of most amorphous polymers is about 10^9 dynes/cm²). Hence, $\tau = \eta/G = 10^4$ s. The result obtained differs from the so-called standard definition of T_g as the temperature at which the relaxation time is equal to 10^2 s. If acoustic measurements are carried out even at very low frequencies ($f \approx 1$ Hz), in this case too at T_g the condition $\omega\tau = N$ is fulfilled at $N \gg 1$.

It is clear that the temperature which corresponds to a mechanical or dielectric loss peak cannot, as a rule, be treated as T_g since such peaks appear when the condition $\omega\tau = 1$ is satisfied. Thus, the peaks in the temperature dependence of dynamic, mechanical or dielectric losses occur at $T_m \geq T_g$.

The values of the glass temperature found from acoustic, dielectric and other physical measurements, in which use is made of periodically varying fields applied to the polymer, may be dependent on the frequency ω of variation of these fields and may increase with increasing ω . This dependence is associated with the phenomenon of "mechanical" glass transition (4). The "mechanical" glass transition is due to the relaxational nature of the transition from the rubbery to the glassy state. In accordance with this, the value of any parameter (measured on periodic loading) that characterizes the relaxation process is determined by the product $\omega\tau$ or by the Deborah number $D = \tau/t$ (where τ is the relaxation time and t is the time of observation). From the point of view of relaxation concepts the difference between an amorphous solid and a liquid can be expressed quantitatively with the aid of the Deborah number. For liquids with very short relaxation times the Deborah number $D \ll 1$, and for amorphous solids $D \gg 1$.

In periodic loading the role of the observation time is played by the period of vibrations T of the field applied to the polymer. Obviously, to the glass-transition temperature there must correspond a quite definite value of $D > 1$. Since at T_g the product $\omega\tau = 2\pi D \gg 1$, it is obvious that D is also much greater than unity.

If the glass temperature is measured at a sufficiently high frequency (at a small period T), the parameter measured (say, the sound velocity), from which T_g is determined, will correspond to the value of $D = N/(2\pi) = \omega\tau/(2\pi)$ (where N is a fixed quantity) at a temperature higher than T_g . Evidently, if at T_g the number D must have quite a definite value, then with increasing frequency ω (with

decreasing period T) there must be observed a decrease in the relaxation time τ , which may be considered, at a first approximation, to be exponentially dependent on the temperature:

$$\tau = A \exp \frac{U}{RT} \quad (3.54)$$

where A is a certain constant; U is the energy of activation.

From formula (3.54) it follows that τ decreases with increasing temperature T . Hence, when any of the physical properties of polymers, which are dependent on the loading frequency, are measured, at high frequencies the parameters that characterize these properties will assume values typical for T_g at higher temperatures. This is precisely what we call "mechanical" glass transition. The dependence of the glass-transition temperature on the frequency at which measurements are carried out (or on the rate of variation of temperature) and also an increase in T_g with increasing frequency (or with increasing rate of heating) is undoubtedly an indication of the kinetic, relaxational nature of the glass transition.

3.3.2. Theories of the Glass Transition

The kinetic approach to the problem of the glass transition has been theoretically substantiated in the works of Volkenshtein and Ptitsyn (25-28), who advanced a phenomenological theory of the glass transition. They considered a system composed of identical kinetic units, which can exist in states 1 and 2. Let the concentration of such kinetic units (expressed in mole fractions) be n_1 in state 1 and n_2 in state 2. It is evident that $n_1 + n_2 = 1$. The rate of change of the concentration n_1 upon transition of the kinetic units from state 1 to state 2 is given by the following kinetic equation:

$$\frac{dn_2}{dt} = -\frac{dn_1}{dt} = W_{12}n_1 - W_{21}n_2 \quad (3.55)$$

where W_{12} and W_{21} are the probabilities of the transitions $1 \rightarrow 2$ and $2 \rightarrow 1$.

The relaxation time is determined by the relation $\tau = (W_{12} + W_{21})^{-1}$. The solution of the kinetic equation (3.55) with account taken of a number of assumptions leads to the following relation in the presence of a single relaxation process:

$$\left(\frac{d\tau}{dT} \right)_{T=T_g} = \left(\frac{dT}{dt} \right)_{T=T_g}^{-1} \quad (3.56)$$

where τ is the relaxation time; T is the absolute temperature; t is the time; $q = dT/dt$ is the rate of cooling.

The relaxation time in this case is given by a formula of the type (3.54):

$$\tau = A \exp \frac{U}{kT} \quad (3.57)$$

If the cooling occurs uniformly, then at $T = T_g$ we have:

$$\frac{AU}{kT_g^2} \exp \frac{U}{kT} = \frac{1}{q} \quad (3.58)$$

Taking the logarithm of Eq. (3.58), we obtain:

$$\ln \frac{AU}{kT_g^2} + \frac{U}{kT_g} = \ln \frac{1}{q} \quad (3.59)$$

From this it follows that the glass-transition temperature must approximately be linearly dependent on the rate of cooling q . Expression (3.58) leads directly to the basic relation for the glass temperature derived by Bartenev (4):

$$q\tau = C \quad (3.60)$$

where $C = kT_g^2/U$. Sometimes relation (3.60) is regarded as a mathematical definition of the glass-transition temperature. Though the theory of the glass transition proposed by Volkenshtein and Ptitsyn has a number of merits, it nevertheless suffers from some serious drawbacks. This theory does not take account of the cooperativeness of segmental motion upon glass transition since it treats the transition of a kinetic unit from one state to another as an individual, independent process. The segmental motion during the glass transition is in fact cooperative: for one of the segments to change its position it is necessary that the position of its neighbours be changed.

Another attempt to explain the glass transition of polymers has been made by Zhurkov (29, 30), who presumed that in the glassy state there are formed non-chemical cross-links between neighbouring polymeric chains which are due to the interaction of functional groups. In this treatment of the glass transition process the most important role is played by the intermolecular interaction. Zhurkov has shown that when the energy of intermolecular interaction increases (say, with increasing number of polar groups in the polymeric chain), the glass temperature increases. On the other hand, when a polar plasticizer is added to a polar polymer, some of the polar groups of the polymer will be blocked off by the plasticizer molecules, and the effectiveness of intermolecular interaction and, hence, the glass temperature will decrease.

The mechanism and nature of the glass transition have been elucidated most completely by Gibbs and DiMarzio (24) and by Adam and Gibbs (31).

3.3.2.1. The Gibbs-DiMarzio Theory

Gibbs and DiMarzio (21) have critically analysed the difficulties that arise in the kinetic approach to the problem of the glass transition. In their opinion, one of the difficulties that arise in the kinetic approach is the anomalous behaviour of some of the thermodynamic parameters upon transition from the rubbery to the glassy state. Indeed, Kauzmann (32) pointed out that if the parameters that characterize the thermodynamic properties measured above T_g are extrapolated to the region of temperatures lower than T_g for the purpose of studying the expected equilibrium behaviour at $T < T_g$, there will be obtained absurd results, say negative values of the entropy.

Another shortcoming of the kinetic approach, in the opinion of Gibbs and DiMarzio, is that the kinetic phenomena cannot be explained from the kinetic viewpoint. These authors maintain that the concept of the equilibrium (metastable) structure of a super-cooled liquid phase resulting from the glass transition is a necessary premise for the understanding of the viscoelastic and dielectric properties of polymers in this region. The theory proposed by Gibbs and DiMarzio rests on the application of a lattice model similar to the Meyer-Flory-Huggins lattice model. The only difference is that Gibbs and DiMarzio maintain that chain stiffness results only from the interaction of the closest fragments situated along the polymeric chain. In their treatment, at a first approximation, no account is taken of the fact that the restriction of the rotation about any of the bonds depends on the conformation of the other molecules. Thus, these authors make use of an approximation in which the number of intramolecular energy parameters is reduced to one.

Gibbs and DiMarzio consider a system made up of n_x chains of a linear polymer, each consisting of x monomer units. Here the term "monomer" is taken to mean a certain structural unit capable of occupying a single definite position in the lattice. Usually this is a single atom in the main chain with side groups attached to it providing these groups are sufficiently small. Further, they assume that any chain conformation is possible in the lattice, whose points have a size not exceeding the size of one unit. It is presumed that the lattice contains vacancies, the number of which is n_0 . If the number of primary valences of each atom in the main chain is z (say, for carbon $z = 4$), then the number of possible (predominantly, low-energy) orientations of the valence bonds is $z - 1$. It is assumed that the energy ε_1 corresponds to one of these orientations, and the energy ε_2 corresponds to each of the $z - 2$ remaining orientations. The total intramolecular energy, which characterizes the chain flexibility, may then be represented in the form

$$E = f\varepsilon_2 (x - 3) n_x + (1 - f) \varepsilon_1 (x - 3) n_x \quad (3.61)$$

where f is the number of bonds "flexed", i.e., bonds whose orientations correspond to the energy ε_2 .

The intermolecular energy (the energy of formation of "holes") proportional to the number of van der Waals bonds will be given by

$$\Phi = 0.5z'\alpha n_0 S_x' \quad (3.62)$$

where α is the interaction energy (the van der Waals energy) of a pair of adjacent but chemically nonbonded links; S_x is a certain function of z' , x , n_x and n_0 ; z' is the coordination number of the most perfect lattice which characterizes the amorphous packing in the chain-hole system.

In the case of the lattice model z' is not necessarily equal to z . Since the coordination number z of the lattice is the total number of bonds possible between a particular unit and the units in the neighbouring lattice points, it follows that $z \geq z'$.

The thermodynamic properties of this system can be determined by considering a canonical ensemble of such systems and the distribution function. First the partition function and then the basic thermodynamic functions are found. While analysing the expression for the free energy and entropy, Gibbs and DiMarzio came to the conclusion that below the experimentally measured glass temperature T_g there must exist a certain temperature T_2 at which (and below which) the conformational entropy of the polymer is equal to zero. They established that this temperature must depend on the energy difference $\varepsilon_2 - \varepsilon_1$ (for *gauche*- and *trans*-isomers), the energy of hole formation α and the molecular mass of the polymer. While considering a real polymeric system which passes through the point T_2 at which the conformational entropy $S = 0$, Gibbs and DiMarzio (21) note that at high temperatures (when $S > 0$) there will be many ways for the molecules to be packed in the amorphous phase. At these temperatures no one macromolecular conformation is preferred over another. When the polymer is cooled, the macromolecular energy falls and the transition from the rubbery to the glassy state is accompanied by two processes: (1) low-energy molecular conformations start to predominate (f decreases), which makes the chains more rigid; (2) the volume decreases (n_0 decreases, which is equivalent to a decrease in the free volume).

When the temperatures $T \leq T_2$ are reached, the attainment of the amorphous state of the polymer would be impossible if these processes continued. Hence, the system retains one of the lowest-energy configurations corresponding to the "principal" state of the amorphous polymer. Gibbs and DiMarzio believe that their theory agrees well with experiment. For example, the theoretical dependence of T_g on molecular mass obtained by these authors for polystyrene practically coincides with the experimentally found dependence. They note that T_g depends slightly on α and is mainly determined

by the parameter $\varepsilon_2 - \varepsilon_1$, which characterizes the stiffness of the polymeric chain. The value of the parameter $\varepsilon_2 - \varepsilon_1$ for stiff chains is always greater than that for flexible chains. From the theory it follows that if the values of $\varepsilon_2 - \varepsilon_1$ are approximately equal for two linear polymers having the same molecular mass, it is possible to determine which of these has a higher glass-transition temperature if the "free volume" n_0 is known. Thus, the Gibbs-DiMarzio theory predicts (true, within certain limits) the dependence of T_g on the free volume (or on the packing density). This agrees, to a certain degree, with the empirical methods of calculation of the glass temperature based on the computation of the macromolecular packing factor through the use of atomic increments in the volume (33, 34).

A weak point in the Gibbs-DiMarzio theory is the statement that the transition to the glassy state, which, according to theory, must occur at the temperature $T_2 < T_g$ is an equilibrium second-order phase transition. The idea of the kinetic nature of the transition from the rubbery to the glassy state is perhaps the most thoroughly substantiated one. Meanwhile, attempts to detect experimentally the temperature T_2 which figures in the Gibbs-DiMarzio theory (it is assumed that $T_2 \approx T_g - 50$ K) have been made up to the present time (see, for example, ref. 4). Though the main trend in the Gibbs-DiMarzio theory is to prove that below the experimentally determinable temperature T_g there must exist a certain temperature T_2 at which the configurational entropy vanishes, giving a true second-order phase transition at this point, the importance of the theory does not lie in this.

The Gibbs-DiMarzio theory is the first physical theory of the glass transition based on the use of the statistical mechanics of polymers. It discloses the molecular mechanism of the glass transition, demonstrating that the transition from the rubbery to the glassy state and the position of the glass-transition temperature are governed by two parameters: the energy difference $\varepsilon_2 - \varepsilon_1$ between *gauche*- and *trans*-isomers and the energy of hole formation α , i.e., the energy of intermolecular interaction.

The Gibbs-DiMarzio theory has exerted a strong impact on investigations devoted to the nature and molecular mechanism of the glass transition. Eisenberg and Saito (35), for example, have shown that within certain limits one may say that the Gibbs-DiMarzio theory is experimentally equivalent to the free-volume theory. Adam and Gibbs (31) have utilized the ideas of the Gibbs-DiMarzio theory for describing the temperature dependence of the relaxation time upon glass transition. They assumed that the dependence of τ on temperature in the transition region is determined by the change of the dimensions of the cooperatively rearranging regions. It has been shown that the size of these regions may be described in terms of the configurational entropy.

The cooperatively rearranging regions are treated as a subsystem of the sample in which enthalpy fluctuations are likely to occur. It is presumed that cooperative rearrangements are possible in the fixed subsystem, depending on its dimensions. It is assumed that each subsystem interacts only with the macroscopic system. The temperature dependence of the relaxation time of segmental motion in the glass transition region is expressed, according to Adam and Gibbs, by the following relation:

$$\tau = A \exp [Z^* (\Delta F)/kT] = A \exp [N_0 s_c^*/S_c kT] \quad (3.63)$$

where A is a certain constant which is practically independent of the temperature; ΔF is the free energy required for reorientation per repeating unit of the chain; Z^* is the smallest size of the cooperative region ($Z^* = N_0 s_c^*/S_c$, where N_0 is Avogadro's number; s_c^* is the critical configurational entropy of the smallest subsystem capable of taking part in the cooperative transition; S_c is the molar configurational entropy of the macroscopic sample).

Formula (3.63) enables one to estimate quantitatively the variation of the glass-transition temperature of the amorphous regions of crystalline polymers with a change in the degree of crystallinity. Indeed, as has already been mentioned, an increase in the degree of crystallinity results in some extension of two-phase chains in the amorphous regions. The extended chains are characterized by a lower entropy, which leads to a decrease in the value of S_c with increasing degree of crystallinity. From formula (3.63) it follows that as the value of S_c decreases the relaxation time increases. An increase in τ will naturally result in an increase in T_g . Obviously, even a slight change in S_c can lead to large changes in τ , since the relaxation time depends on S_c by an exponential law. The Adam-Gibbs theory provides a satisfactory description of the change of the relaxation time of segmental motion and of the glass-transition temperature of amorphous regions caused by a change in the degree of crystallinity of crystalline polymers.

This theory has also made it possible to derive theoretically the well-known empirical Williams-Landell-Ferry equation, which describes the temperature dependence of the relaxation time of segmental motion at $T > T_g$.

References

1. Vinogradov, G. V. and A. Ya. Malkin, *Rheology of Polymers* (translated by Artavaz Beknazarov), Mir Publishers, Moscow and Springer-Verlag, Berlin-Heidelberg-New York, 1980.
2. Lodge, A., *Elastic Liquids*, Academic Press, New York, 1964.
3. Middleman, S., *The Flow of High Polymers*, Wiley Interscience, New York, 1968.
4. Bartenev, G. M. and Yu. V. Zelenev, *A Course of Polymer Physics*, Khimiya, Moscow, 1976 (in Russian).

5. Tager, A. A., *Physical Chemistry of Polymers* (translated by D. S. Sobolev), Mir Publishers, Moscow, 1972.
6. Kuhn, W., *Koll.-Z.*, **76**, 3, 258 (1936).
7. Kuhn, W., *Koll.-Z.*, **68**, 1, 2 (1934).
8. Wall, F. T., *J. Chem. Phys.*, **10**, 2, 132 (1942).
9. Kobeko, P. P., *Amorphous Substances*, Izd. Akad. Nauk SSSR, Leningrad, 1952 (in Russian).
10. Wall, F. T., *J. Chem. Phys.*, **10**, 7, 485 (1942).
11. Wall, F. T., *J. Chem. Phys.*, **11**, 11, 527 (1943).
12. Flory, P., and J. Rehner, *J. Chem. Phys.*, **11**, 11, 512 (1943).
13. Flory, P., *Chem. Rev.*, **35**, 1, 51 (1944).
14. James, H. and E. Guth, *J. Polymer Sci.*, **4**, 153 (1949).
15. James, H. and E. Guth, *J. Chem. Phys.*, **11**, 10, 455 (1943).
16. Treloar, L. R. G., *The Physics of Rubber Elasticity*, 2nd ed., Clarendon Press, Oxford, 1960.
17. Ferry, J. D., *Viscoelastic Properties of Polymers*, John Wiley and Sons, Inc., New York, 1970.
18. Ward, I. M., *Mechanical Properties of Solid Polymers*, Wiley-Interscience, London, 1971.
19. Perepechko, I. I., *Acoustic Methods of Investigating Polymers* (translated by G. Leib), Mir Publishers, Moscow, 1975.
20. Porter, R. and J. Johnson, *J. Chem. Rev.*, **66**, 1, 1 (1966).
21. Gibbs, J. H. and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 3, 373 (1958).
22. Frenkel, S. Ya. and G. K. Elyashevich, *Vysokomol. Soedin.*, **A**, **13**, 2, 493 (1971).
23. Perepechko, I. I. and O. V. Startsev, *Akust. Zhurn.*, **22**, 5, 749 (1976).
24. Staverman, A., *J. Rheol. Acta*, **5**, 4, 283 (1966).
25. Volkenshtein, M. V., *Molecular Biophysics*, Nauka, Moscow, 1973 (in Russian).
26. Volkenshtein, M. V. and O. B. Ptitsyn, *Doklady Akad. Nauk SSSR*, **103**, 5, 795 (1955).
27. Volkenshtein, M. V. and O. B. Ptitsyn, *Zhurn. Tekh. Fiz.*, **26**, 10, 2204 (1956).
28. Volkenshtein, M. V., *Configurational Statistics of Polymer Chains*, Interscience, New York, 1963.
29. Zhurkov, S. N., *Doklady Akad. Nauk SSSR*, **47**, 7, 493 (1945).
30. Zhurkov, S. N., *Doklady Akad. Nauk SSSR*, **49**, 3, 201 (1945).
31. Adam, G. and J. H. Gibbs, *J. Chem. Phys.*, **43**, 1, 139 (1965).
32. Kauzmann, W., *Chem. Rev.*, **43**, 2, 219 (1948).
33. Yarosh, A. A., A. A. Askadsky, and S. P. Krukovsky, *Vysokomol. Soedin.*, **16**, 3, 527 (1974).
34. Van Krevelen, D. W., *Properties of Polymers. Correlation with Chemical Structure*, Elsevier Publ. Co., Amsterdam-London-New York, 2nd ed., 1976.
35. Eisenberg, A. and Sh. Saito, *J. Chem. Phys.*, **45**, 5, 1673 (1966).

Chapter 4

Thermal Properties of Polymers

4.1. Heat Capacity of Polymers

4.1.1. Basic Concepts of the Heat Capacity of Solids

Heat capacity is one of the most important thermal characteristics of substances. It is defined as the amount of heat that must be imparted to a body to raise its temperature by 1°C . The heat capacity C per one mole of substance is called the molar heat capacity. In theory, most frequently the heat capacity of a system is considered at constant volume, C_v , which is substantially dependent on temperature.

The molar heat capacity of a solid at constant volume, C_v , is defined by the expression

$$C_v = \left(\frac{\partial U_m}{\partial T} \right)_v \quad (4.1)$$

where U_m is the internal energy of 1 mole of substance; T is the temperature.

We know that a solid consists of atoms which oscillate about an equilibrium position. In the classical approximation, the atoms of a solid may be regarded as harmonic oscillators. This means that the oscillating atoms experience forces of interaction which obey Hooke's law, i.e., these forces are proportional to the relative departure of the atoms from their mean equilibrium positions.

We know that the average energy of a simple one-dimensional harmonic oscillator, E_1 , depends only on temperature:

$$\langle E_1 \rangle = kT \quad (4.2)$$

The Boltzmann constant, $k = 1.38 \times 10^{-23}$ J/K, is defined as the ratio $k = R/N_0$, where R is the universal gas constant [$R = 8.31$ J/(mole·K)], and N_0 is Avogadro's number ($N_0 = 6.023 \times 10^{23}$ mole $^{-1}$). One mole of a solid can be treated as a system of $3N_0$ simple one-dimensional harmonic oscillators. The internal energy of such a system is given by

$$U_m = 3N_0 kT = 3RT \quad (4.3)$$

From expression (4.1) it follows that the molar heat capacity of a solid is

$$C_v = 3R \approx 0.025 \text{ kJ/(mole}\cdot\text{K)} \quad (4.4)$$

Expression (4.4) is the well-known Dulong-Petit law, which is in good agreement with the values of C_v found experimentally for

many solids over a wide range of temperatures, up to quite high temperatures.

It has, however, been found that at low temperatures the heat capacity of solids depends on temperature, which contradicts the Dulong-Petit law, and that with a considerable decrease of temperature, when $T \rightarrow 0$, the heat capacity of non-metallic solids decreases with decreasing temperature. This result cannot be explained within the framework of the classical theory. One of the first to pay attention to this was Einstein.

4.1.1.1. The Einstein Theory

Einstein attempted to account for a sharp decrease in the heat capacity of solids at low temperatures (at $T \rightarrow 0$) by proceeding from a simple model. In order to explain thermal properties at low temperatures, Einstein suggested that the crystal lattice of a solid containing N vibrating atoms be regarded as a system of $3N$ independent one-dimensional harmonic oscillators, each with the same characteristic vibrational frequency, ν . The Einstein harmonic oscillators differ from classical harmonic oscillators, since while a classical harmonic oscillator can have any vibration amplitude and, hence, any energy, Einstein's quantum harmonic oscillators can have only strictly defined, discrete energy values. The magnitude of this energy is given by the Planck formula:

$$E = nh\nu \quad (4.5)$$

where $n = 0, 1, 2, \dots$ (positive integers); h is Planck's constant ($h = 6.62 \times 10^{-34}$ J.s); ν is the frequency.

Formula (4.5) is sometimes written in the form:

$$E = n\hbar\omega \quad (4.6)$$

where $\omega = 2\pi\nu$ is the circular frequency; $\hbar = h/2\pi$.

Thus, a quantum harmonic oscillator can have only quantized energy values which differ by the value of n . In accordance with quantum theory, the average energy of a harmonic oscillator can be represented in the following form:

$$\langle E_1 \rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega e^{-\frac{n\hbar\omega}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{kT}}} = \frac{\hbar\omega (e^{-\frac{\hbar\omega}{kT}} + 2e^{-2\frac{\hbar\omega}{kT}} + \dots)}{(1 + e^{-\frac{\hbar\omega}{kT}} + e^{-2\frac{\hbar\omega}{kT}} + \dots)} \quad (4.7)$$

Expression (4.7) can be transformed so that

$$\langle E_1 \rangle = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \quad (4.8)$$

A comparison of expressions (4.8) and (4.2) shows that the average energies of quantum and classical harmonic oscillators are substantially different. Note that expression (4.8) is more general. From this expression we can derive, as a special case, an expression for the average energy of a classical harmonic oscillator. Indeed, at high temperatures, when $kT \gg \hbar\omega$, the denominator in expression (4.8) can be expanded into a series:

$$e^{\frac{\hbar\omega}{kT}} - 1 = 1 + \frac{\hbar\omega}{kT} + \dots - 1 \approx \frac{\hbar\omega}{kT}$$

Thus, at high temperatures expression (4.8) has the form

$$\langle E_1 \rangle \approx kT$$

The heat capacity of a system of N identical quantum harmonic oscillators can be written thus:

$$C = \frac{\partial U}{\partial T} = \frac{\partial (N \langle E_1 \rangle)}{\partial T} = Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} \quad (4.9)$$

Expression (4.9) can also be written in a somewhat different form if one makes use of the concept of the characteristic Einstein temperature θ_E , which is defined by the equation

$$\hbar\omega = k\theta_E \quad (4.10)$$

For most solids the characteristic temperature, θ_E , is equal to about 100-300 K. From formula (4.10) it follows that at $\theta_E = 300$ K the characteristic frequency $\nu = \omega/2\pi = k\theta_E/h \approx 5 \times 10^{12}$ Hz. This frequency approximately corresponds to the vibrational frequency of individual atoms. In view of formula (4.10), the expression for heat capacity (4.9) can be written as follows:

$$C = Nk \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} = NkE \left(\frac{\theta_E}{T} \right) \quad (4.11)$$

where $E \left(\frac{\theta_E}{T} \right)$ is the Einstein function defined as

$$E \left(\frac{\theta_E}{T} \right) = \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (4.11a)$$

Formula (4.11) describes well the temperature dependence of the heat capacity of some solids.

In the case of low temperatures, when $T \rightarrow 0$ (i.e., at $kT \ll \hbar\omega$) and $T \ll \theta_E$, from formula (4.11) it follows that

$$C \approx Nk \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad (4.12)$$

It is obvious that the largest contribution to the temperature dependence of heat capacity at $T \rightarrow 0$, according to the Einstein theory, is made by the exponential factor. From formula (4.12) we see that at low temperatures the heat capacity must decrease according to an exponential law. Numerous experimental data, however, indicate that the heat capacity of the crystal lattice of most solids at $T \rightarrow 0$ varies proportionately to T^3 . This fact has been accounted for in the Debye theory.

4.1.1.2. The Debye Theory

The Einstein postulate that all atoms may be regarded as harmonic oscillators vibrating with the same frequency would have been satisfactory if each atom had vibrated independently of its neighbours. In actual fact, the atoms of a solid are so firmly bound with one another that most probably they vibrate as an entity. Debye proposed that a solid be treated as an elastic continuum and derived an expression for vibrational frequencies that would be present in such a system. The discrete nature of the crystal lattice and its atomic structure were taken into account only by way of limiting the number of possible vibrational frequencies in the lattice to the $3N$ degrees of freedom of the N atoms making up the crystal lattice. Debye suggested that the acoustical spectrum of a solid be regarded as the spectrum of an isotropic homogeneous elastic continuum, but that the number of independent elastic waves that arise as a result of the oscillations of N lattice atoms be assumed to be equal to $3N$. It is known that in an isotropic elastic continuum for each wave vector \vec{k} there correspond one longitudinal wave and two transverse waves with speeds independent of the direction of their propagation.

The internal energy in Debye's theory is defined by the following expression:

$$U = \frac{3k^4 T^4}{2\pi^2 \hbar^3 \bar{c}^3} \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad (4.13)$$

where \bar{c} is the average velocity of elastic waves; $x_m = \hbar \omega_m / (kT)$ (here ω_m is the maximum frequency of lattice vibrations, which is governed by the condition that the number of possible lattice vibrations is equal to $3N$).

It is known that

$$\omega_m = \bar{c} \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (4.14)$$

where N is the number of atoms in volume V . The average speed of elastic waves in an isotropic elastic solid is

$$\bar{c} = \left[\frac{1}{3} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \right]^{-1/3} \quad (4.15)$$

in which expression the quantities c_t and c_l are the average speeds of transverse and longitudinal elastic waves, respectively.

We now introduce the notation

$$\hbar\omega_m/k = \theta_D \quad (4.16)$$

The parameter θ_D is called the Debye characteristic temperature and plays an important part in the consideration of the thermal properties of a solid. From expressions (4.14) through (4.16) it follows that

$$\theta_D = \frac{h}{k} \left(\frac{3N}{4\pi V} \right)^{1/3} \left[\frac{1}{3} \cdot \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \right]^{-1/3} \quad (4.17)$$

Differentiating the expression for the internal energy with respect to temperature, we obtain the following expression for heat capacity at constant volume (1, 2):

$$C_v = 9N_1 k \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_m} \frac{e^x x^4 dx}{(e^x - 1)^2} \quad (4.18)$$

where $N_1 = N/V$ is the number of atoms per unit volume.

The expression for heat capacity can be written in a different form:

$$C_v = 3N_1 k D \left(\frac{\theta_D}{T} \right) \quad (4.19)$$

where D (θ_D/T) is the Debye function equal to

$$D \left(\frac{\theta_D}{T} \right) = 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{\left(\frac{\theta_D}{T} \right)^4 e^{\theta_D/T} dx}{(e^{\theta_D/T} - 1)^2} \quad (4.20)$$

The Debye function cannot be calculated accurately and therefore use is made of various approximations. Approximate methods of calculation are considerably simplified in the case of high ($T \gg \theta_D$) and very low ($T \ll \theta_D$) temperatures.

At $T \gg \theta_D$ (i.e., at $x_m \ll 1$), from expression (4.18) we have

$$C_v \approx 3R \quad (4.21)$$

which is in good accord with the Dulong-Petit law.

At very low temperatures, when $T \ll \theta_D$ (at $T < \theta_D/12$), from expression (4.18) we can obtain, with an accuracy of up to 1 per cent, the following expression for heat capacity:

$$C_v = \frac{12\pi^4 Nk}{5} \left(\frac{T}{\theta_D} \right)^3 = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_D} \right)^3 \quad (4.22)$$

This formula is the well-known Debye cube law. It agrees well with experimental data for a large number of solids. The question of the

limits of applicability of Debye's equation has not, however, been resolved completely. In fact, formula (4.22) is in good agreement with experimental data not at $T < \theta_D/12$ but at much lower temperatures. The heat capacity of real solids is usually described well by Debye's equation only at $T \leq \theta_D/50$ and sometimes at $T \leq \theta_D/100$. For polymers the Debye T-cube law holds, as a rule, only in a very narrow range of temperatures only a few degrees above 0 K.

The good agreement between Debye's theory and experimental data at very low temperatures is ascribed to the fact that at $T \rightarrow 0$ K the crystal lattice experiences oscillations of sufficiently long wavelength, much larger than the lattice parameters.

It should be noted that Debye's theory has a number of shortcomings. For instance, it assumes that all the elastic waves in the lattice travel at the same speed. The dispersion law used in the derivation of relation (4.22) has the form $\omega = \bar{c}K$, where $K = 2\pi/\lambda$ is the wavenumber. Thus, Debye's theory disregards the dispersion (frequency dependence) of the speed of elastic waves. In accordance with this, in Debye's theory it is assumed that the maximum frequency ω_m for all the waves excited in the lattice is the same, which does not conform with the actual picture observed in real solids. Moreover, the Debye theory ignores the actual nature of the interaction between the atoms and molecules of which the solid is composed.

Thus, the Debye theory is concerned with the complicated motion of the mass centres of the interlinked N elements of the lattice. This complex motion (lattice oscillations) is assumed to be equivalent to the motion of $3N$ independent one-dimensional harmonic oscillators. The coordinates of these oscillators are called the normal coordinates and their oscillations are known as normal vibrations. The internal energy and heat capacity of a solid is additively composed of the contributions from individual normal vibrational modes. To calculate the heat capacity (to derive the formula describing the dependence of heat capacity on temperature), it is necessary to know the frequency spectrum of normal vibrations. This spectrum can be computed theoretically by making use of the so-called secular equation. In the case of a simple lattice, the solution of the secular equation contains three frequency branches (acoustical branches) which correspond to three possible independent orientations of the vector of polarization of lattice waves, i.e., to three types of elastic waves excited in the lattice (two transverse waves and one longitudinal wave). The simplicity of the Debye equation results from a number of simplifications made in its derivation.

The atomic structure of solids has been taken into considerably greater account in the theory of heat capacity proposed by Born and von Kármán (3). In this theory, a solid is regarded as a lattice consisting of point masses interconnected by springs. Born and von

Kármán not only considered the action of central forces but also made an attempt to take into account the forces operating between atoms at greater distances. They showed that in the case of the simplest model, which is a one-dimensional chain with central forces acting between the nearest neighbouring atoms (nearest-neighbour forces), the Debye assumption that no dispersion of the speeds of elastic waves is present is not valid. The Born-Kármán theory takes into account that the maximum frequency ω_m (the cutoff frequency of the spectrum of normal vibrations) must be different for each elastic wave in each direction.

The theory allows the calculation of the temperature dependence of heat capacity if the model of interatomic forces is known. In a number of simple cases theoretical computations are in good agreement with the results of experimental investigations. But calculation of the frequency spectrum, which must be known if one wishes to derive a general formula for heat capacity appears to be a very difficult task. For this to be done, one has to know all the force constants and the interaction potential between atoms. Even then the solution of the secular equation is found to be rather involved. Besides, in real solids one has to deal with complex lattices. If the unit cell of such a lattice consists of n structural elements, one must add to the acoustical branches that result from the solution of the secular equation 3 ($n - 1$) optical branches, which under certain conditions are separated from one another and from the acoustical branches by energy gaps. All this considerably complicates the calculation of the spectrum of normal vibrations.

In view of this, the Debye theory is used most frequently in a study of the thermal properties of solids at low temperatures.

In Debye's theory it is assumed that the energy of each normal mode of vibration, E_i , is quantized:

$$E_i = n_i \hbar \omega_i \quad (4.23)$$

where n_i are whole numbers.

Thus, each normal mode of vibration (or each elastic wave) may be treated in the Debye theory like a quasi-particle characterized by strictly defined, discrete values (quanta) of energy. From the standpoint of quantum theory, normal lattice vibrations (the Debye elastic waves) may be regarded as quasi-particles which are energy quanta of the field of elastic vibrations, that is, phonons.

In the quantum theory of heat capacity, lattice oscillations are treated as the phonon gas, which also leads to the Debye equation. By analogy with the kinetic theory of gases, solid-state quantum theory deals with such concepts as the mean free path of phonons, the interaction of phonons, etc. The concept of the elastic waves in the lattice being quasi-particles (phonons), a concept which appeared as the result of the development of the Debye theory of heat capacity,

has proved fruitful and is widely used in modern solid-state physics. It will be shown later that many phenomena that appear in polymers at low temperatures are phononic in nature.

4.1.2. Theories of the Heat Capacity of Polymers

According to Debye's theory, formula (4.22) should be valid for solids at $T < \theta_D/12$. The results of experimental investigations of the heat capacities of polymers at low temperatures (4) show, however, that, even with this condition being fulfilled, above 5-10 K the Debye equation fails to describe the temperature dependence of C_v even qualitatively. This is associated with the neglect in the Debye theory of the anisotropy of the forces of interatomic interaction in polymeric chains. One of the first theories of heat capacity that could be used to describe the thermal properties of polymers has been proposed by Tarasov.

4.1.2.1. The Tarasov Theory

Tarasov (5-7) applied the basic propositions of Debye's theory, which holds for an isotropic elastic continuum (a three-dimensional continuum), to one-dimensional and two-dimensional continuous media.

In the Debye approximation for a three-dimensional lattice the distribution function of natural frequencies, $\varphi(\nu)$, may be written in the form:

$$\varphi(\nu) = 9N\nu_m^{-3}\nu^2 \quad (4.24)$$

Thus, the distribution function of the frequencies of normal vibrations in a three-dimensional lattice is directly proportional to the square of the frequency ν^2 . The number ds_3 of natural vibrations of a lattice or a three-dimensional continuum in the frequency range ν to $\nu + d\nu$ is given by the expression:

$$ds_3 = \varphi(\nu) d\nu = 9N\nu_m^{-3}\nu^2 d\nu \quad (4.25)$$

Tarasov found that in the case of a two-dimensional continuum, i.e., a planar or surface network of atoms (a vibrating membrane can be used as an analogy), the number of natural vibrations, ds_2 , between frequencies ν and $\nu + d\nu$ will be equal to

$$ds_2 = 6N\nu_m^{-2}\nu d\nu \quad (4.26)$$

With a one-dimensional continuum, i.e., an elastic rod, which represents, to a certain extent, an oscillating chain of atoms in the Tarasov theory, the number of natural vibrations between frequencies ν and $\nu + d\nu$ equals:

$$ds_1 = 3N\nu_m^{-1} d\nu \quad (4.27)$$

In Debye's theory, the number of natural vibrations in the lattice is brought into agreement with the total number of vibrational degrees of freedom ($3N$) of a system consisting of N one-dimensional harmonic oscillators by using the relation:

$$\int_0^{\nu_m} \varphi(\nu) d\nu = 3N \quad (4.28)$$

where $\varphi(\nu)$ is defined by expression (4.24).

Hence, for a three-dimensional continuum

$$\int_0^{\nu_m} ds_3 = 3N \quad (4.28a)$$

By analogy, in the Tarasov theory we also have

$$\int_0^{\nu_m} ds_1 = 3N \quad \text{and} \quad \int_0^{\nu_m} ds_2 = 3N$$

In this case, $3N$ is the total number of vibrational degrees of freedom for a chain or layer.

In a general case, expressions (4.25) through (4.27) may be written in the following form:

$$ds_m = 3mN\nu_m^{-m}\nu^{m-1}d\nu \quad (4.29)$$

where ds_m is the total number of natural modes of vibration in the interval $d\nu$ for an m -dimensional continuum ($m = 3$ in the case of a lattice; $m = 2$ for a layer; and $m = 1$ for a chain).

Using formula (4.29) and expression (4.8) for the average energy of a quantum harmonic oscillator, $\langle E_1 \rangle$, we obtain for the total vibrational energy of an m -dimensional continuum:

$$U_m = \int_0^{\nu_m} \langle E_1 \rangle ds_m \quad (4.30)$$

In turn, the vibrational heat capacity of the m -dimensional continuum is equal to

$$C_m = \frac{\partial U_m}{\partial T} = \frac{\partial}{\partial T} \int_0^{\nu_m} \langle E_1 \rangle ds_m \quad (4.31)$$

Substituting expression (4.8) into formula (4.30) and (4.31) and taking cognizance of relation (4.16), we obtain an equation for

vibrational energy (5):

$$U_m = 3mR \frac{T^{m+1}}{\theta_m^m} \int_0^{\nu_m} \frac{x^m dx}{e^x - 1} \quad (4.32)$$

Making use of expression (4.32) for the case of $m = 3$ (a three-dimensional continuum), Tarasov derived the usual expressions (4.18) through (4.20), which follow from the Debye theory.

For the case of $m = 2$ (a two-dimensional continuum) the following expression obtains for the heat capacity:

$$C_v = 3N_1 k D_2 \left(\frac{\theta_2}{T} \right) \quad (4.33)$$

where D_2 (θ_2/T) is the Debye two-dimensional function. This function is defined as

$$D_2 \left(\frac{\theta_2}{T} \right) = 2 \left(\frac{T}{\theta_2} \right)^2 \int_0^{\theta_2/T} \frac{\left(\frac{\theta_2}{T} \right)^3 e^{\theta_2/T} d \left(\frac{\theta_2}{T} \right)}{(e^{\theta_2/T} - 1)^2} \quad (4.34)$$

For a one-dimensional continuum ($m = 1$)

$$C_v = 3N_1 k D_1 \left(\frac{\theta_1}{T} \right) \quad (4.35)$$

where θ_1 is the characteristic temperature (for $m = 1$); D_1 (θ_1/T) is the Debye one-dimensional function defined as

$$D_1 \left(\frac{\theta_1}{T} \right) = \frac{T}{\theta_1} \int_0^{\theta_1/T} \frac{\left(\frac{\theta_1}{T} \right)^2 e^{\theta_1/T} d \left(\frac{\theta_1}{T} \right)}{(e^{\theta_1/T} - 1)^2} \quad (4.36)$$

Using the approximate values of the integrals at $\theta_m/T \gg 1$, the equations for the heat capacities of chains, layers, and lattices can be represented in the form (5):

$$C_1 = \pi^2 R \left(\frac{T}{\theta_1} \right) \quad (4.37)$$

$$C_2 = 43.272 R \left(\frac{T}{\theta_2} \right)^2 \quad (4.38)$$

$$C_3 = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_3} \right)^3 \quad (4.39)$$

The characteristic temperatures θ_1 and θ_2 are connected with the Debye temperature $\theta_D = \theta_3$ by the relations $\theta_1 = 1.5 \theta_D$ and $\theta_2 = 1.125 \theta_D$.

Equations (4.37) and (4.38) have been specifically derived for describing the temperature dependence of the heat capacities of solids whose structures are built of chains or layers with atoms

bonded very firmly (say, by the primary valence bonds). This is on the condition that the interaction between chains or between layers themselves is weaker (for example, the interaction due to van der Waals forces). This version of the heat-capacity theory proposed by Tarasov has come to be known as the theory of non-interacting chains or layers.

An essential feature of the equations given above is that they are intended for the calculation of the heat capacities of solids having a lamellar or chain-like (as in the case of polyethylene) structure, in which the forces of interaction between layers or chains are several orders of magnitude lower than in the plane of the layers or along the chains. In the region of very low temperatures, at which the effect of the weak forces of interaction between layers or chains is manifested, the lengths of Debye waves (elastic waves arising in the lattice due to the thermal vibrations of atoms) are still sufficiently great as compared with the distances between the structural elements of the lattice. Here the distribution function of the natural vibrational frequencies of the lattice, $\varphi(\nu)$ (the spectrum distribution density), is proportional to ν^2 and is defined by expression (4.24). Therefore, the heat capacity of solids possessing a lamellar or chain-like structure at very low temperature obeys the Debye T-cube law (the Debye third power law).

As the temperature rises there will come a time when the interaction between layers or chains begins to play a secondary role. The frequency distribution in the vibrational spectrum of such solids degenerates more and more into the frequency distribution typical for a monomolecular layer or a one-dimensional chain.

This change in the character of the temperature dependence of heat capacity has been considered in a more systematic way by Tarasov in a theory of heat capacity which takes into account the interaction of chains and layers. In order to take into account all the intermediate cases, in addition to the limiting cases of the weak interaction, which may be neglected as compared with the interaction inside the chains and layers, Tarasov assumed that in a situation of interacting chains not all the $3N$ modes of vibration, whose frequencies are in the range from ν_{\max} to 0, are distributed by the law of the linear continuum; only a certain number ($3N_1$), corresponding to the frequencies between ν_{\max} and ν_1 , are. Then for a one-dimensional continuum we obtain instead of Eq. (4.27):

$$ds_{\frac{1}{2}}^* = 3N_1 (\nu_{\max} - \nu_1)^{-1} d\nu \quad (4.40)$$

In this case, instead of expressions (4.28) and (4.28a), we must write:

$$\int_{\nu_1}^{\nu_{\max}} ds_{\frac{1}{2}}^* = 3N_1 \quad (4.41)$$

The parameter ν_1 is the limiting vibrational frequency of an atom of a given chain in the force field of surrounding chains. Here it is assumed that the vibrations, to which there correspond frequencies lower than ν_1 (i.e., from 0 to ν_1), are distributed not by the law of the linear continuum [Eq. (4.40)] but by the Debye law or a three-dimensional continuum, which in this particular case takes the form:

$$ds_3 = 9N_2\nu_1^{-3}\nu^2 d\nu \quad (4.42)$$

Obviously, the total number of atoms in the system under consideration is $N = N_1 + N_2$. It follows that the total number of vibrational degrees of freedom of N_2 atoms for which relation (4.42) holds is determined by the following expression:

$$\int_0^{\nu_1} ds_3 = 3N_2 \quad (4.43)$$

Tarasov (5) gives the following expression for the vibrational energy, $U_{1(3)}$, of interacting chains:

$$U_{1(3)} = \frac{3N}{\nu_{\max}} \int_0^{\nu_{\max}} \frac{h\nu d\nu}{e^{\frac{h\nu}{kT}} - 1} d\nu + \frac{9N}{\nu_1^3 \nu_{\max}} \int_0^{\nu_1} \frac{(h\nu)^3}{e^{\frac{h\nu}{kT}} - 1} d\nu \quad (4.44)$$

Making the substitutions $h\nu/(kT) = x$ and $h\nu_1/(kT) = \theta_1$ in Eq. (4.44), we obtain the following formula for the heat capacity of interacting chains:

$$C_{1(3)} = \bar{D}_1\left(\frac{\theta_1}{T}\right) - \frac{\theta_3}{\theta_1} \left[\bar{D}_1\left(\frac{\theta_3}{T}\right) - \bar{D}_3\left(\frac{\theta_3}{T}\right) \right] \quad (4.45)$$

where \bar{D}_1 is the heat-capacity function of a linear continuum for interacting chains; \bar{D}_3 is the ordinary heat-capacity function.

The expression for the heat capacity of interacting layers, $C_{2(3)}$, is deduced in an analogous way:

$$C_{2(3)} = \bar{D}_2\left(\frac{\theta_2}{T}\right) - \left(\frac{\theta_3}{\theta_2}\right)^2 \left[\bar{D}_2\left(\frac{\theta_3}{T}\right) - \bar{D}_3\left(\frac{\theta_3}{T}\right) \right] \quad (4.46)$$

where \bar{D}_2 is the heat-capacity function of non-interacting layers.

From Eqs. (4.45) and (4.46) it follows that the temperature dependence of the heat capacity of a system consisting of interacting layers or interacting chains can be expressed in terms of the characteristic temperatures θ_1 and θ_2 that determine the spectrum of "internal" vibrations of the chains or layers. In calculations, use is also made of the characteristic temperature θ_3 which takes into account the interaction of these vibrations.

At very low temperatures Eqs. (4.45) and (4.46) lead to a cubic dependence of heat capacity on temperature. Indeed, at $T \rightarrow 0$

$$\bar{D}_1\left(\frac{\theta}{T}\right) = \pi^2 R \left(\frac{T}{\theta}\right) \quad (4.47)$$

$$\bar{D}_2\left(\frac{\theta}{T}\right) = 43.272 R \left(\frac{T}{\theta}\right)^2 \quad (4.48)$$

$$\bar{D}_3\left(\frac{\theta}{T}\right) = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta}\right)^3 \quad (4.49)$$

Substituting expressions (4.47) through (4.49) into Eqs. (4.45) and (4.46), we get:

$$C_{1T \rightarrow 0}^{(3)} = \frac{\theta_3}{\theta_1} \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_3}\right)^3 = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_{1,3}}\right)^3 \quad (4.50)$$

$$C_{2T \rightarrow 0}^{(3)} = \left(\frac{\theta_3}{\theta_2}\right)^2 \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_3}\right)^3 = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_{2,3}}\right)^3 \quad (4.51)$$

where

$$\theta_{1,3} = \theta_1^{1/3} \theta_3^{2/3} \quad \text{and} \quad \theta_{2,3} = \theta_3^{1/3} \theta_2^{2/3}$$

From the equations given above it follows that with a substantial difference between the characteristic temperatures, when $\theta_1/\theta_3 \gg \gg 1$ (or when $\theta_2/\theta_3 \gg 1$) there may exist such a temperature region in which C_v is proportional to T (for chains) and C_v is proportional to T^2 (for layers), since the bracketed differences in Eqs. (4.45) and (4.46) are then sufficiently small. When the temperature is lowered further, we see a departure from the dependences $C_v \propto T$ and $C_v \propto T^2$, respectively, and the heat capacity begins to be dependent on temperature according to the T-cube law. Evidently, when the ratio θ_3/θ_1 changes from 0 to 1, there are possible all kinds of dependences of heat capacity on temperature that lie between the functions $C \propto T$ (for the case of non-interacting chains) and the Debye law $C \propto T^3$.

One can hardly expect, however, that the temperature dependence of heat capacity can be fully described by the above equations which take into account the presence of linear or two-dimensional structures with a weak or strong interaction. Just as in the case of the use of the ordinary Debye equation, the spectrum of normal vibrations of a continuum is sometimes combined with one or more vibration frequencies of side groups. Tarasov (5) noted in 1950 that the temperature dependence of the heat capacity of organic polymers can be described by combining the relations derived by him, (4.45) and (4.46) or (4.33) and (4.35), with the Einstein functions for the characteristic frequencies of side groups.

Wunderlich (8) and later Tucker and Rees (9) made use of the Tarasov theory for describing the temperature dependence of the heat

capacity of a number of polymers and showed that this theory is in good agreement with experimental data. Later, however, Baur (4) noted that it remained unclear to what extent this agreement derives from the correctness of the choice of the physical model, since the Tarasov theory, while enabling sufficiently accurate calculations of the spectrum of valence vibrations in the low-frequency region, disregards the spectrum of deformation vibrations.

The Tarasov theory has also been criticized by Lifshitz.

4.1.2.2. The Lifshitz Theory

Lifshitz (10) focused his attention on the fact that Tarasov had ignored some important points arising from the unusual law of dispersion of elastic flexural waves in the limiting case of non-interacting chains and layers. Lifshitz considered anew the question of the dispersion law for the long-wave part of the vibrational spectrum of a lamellar crystal as a whole, using an approximation which, as well as the equations of the theory of elasticity of a strongly anisotropic body, also takes into account the transverse rigidity of atomic layers or chains.

In the case of crystalline structures, which are systems of weakly interlinked lamellae or chains, dispersion laws other than the Debye and Tarasov theories were used for elastic waves. For waves that propagate in non-interacting chains the following relations were obtained:

$$\omega_3 = cK_z \text{ (longitudinal waves)} \quad (4.52)$$

$$\omega_{1,3} = \gamma K_z^2 \text{ (flexural waves)} \quad (4.53)$$

where the z axis coincides with the chain axis; c is the velocity of elastic waves; K_z is the projection of the wave vector onto the z axis; $\gamma = a\bar{v}/\pi$ (a is the interatomic distance in the chain; \bar{v} is the "transverse rigidity" of the chain, a dimensionless parameter).

Taking into account the contributions of both longitudinal and flexural waves to the energy, Lifshitz obtained an expression for the heat capacity of non-interacting chains:

$$C_1 = Nk\gamma_1 \left(\frac{T}{\theta_1} \right)^{1/2} \left\{ 1 + \gamma_2 \left(\frac{T}{\theta_1} \right)^{1/2} \right\} \quad (4.54)$$

where $\gamma_1 \approx 2.3/\sqrt{\bar{v}}$; $\gamma_2 \approx \sqrt{\bar{v}}$; θ_1 is the "longitudinal" Debye temperature.

At low temperatures, when $T \ll \theta$, the heat capacity is equal to

$$C_1 = Nk\gamma_1 \left(\frac{T}{\theta_1} \right)^{1/2} \quad (4.55)$$

Thus, unlike Tarasov who predicts for this case a linear dependence of heat capacity on temperature [Eq. (4.37)], Lifshitz found that C_1

is proportional to \sqrt{T} . For the case of non-interacting layers at $T \ll \theta$ he uses the following relation (10):

$$C_2 = \frac{Nk}{12} \frac{\pi T (a')^2}{\hbar \gamma} \propto Nk \frac{T}{\theta_2} \quad (4.56)$$

where $(a')^2$ is the area of a unit cell in the plane of the layer; $\gamma = ca'$; $\theta_2 = \pi \hbar c / ka'$.

Thus, in the case of interacting layers as well the Lifshitz theory leads to dramatically different results as compared with the Tarasov theory [see Eq. (4.38)].

In order to describe real chain and lamellar structures an attempt has been made (10) to take into account the interaction between chains (or layers). For this purpose, use was made of the law of dispersion of elastic waves in a crystal (11) in which the interaction forces acting in one direction are strongly different from the forces that act in the other two directions. It was assumed that the crystal has an axis symmetry of elastic properties. This is true for crystals having the hexagonal system.

For interacting chains Lifshitz (10) derived the following expressions for heat capacity:

$$C = A \left(\frac{T}{\theta} \right)^3 \quad \text{at} \quad T \ll \eta^2 \theta \quad (4.57)$$

$$C = B \left(\frac{T}{\theta} \right)^{5/2} \quad \text{at} \quad \eta^2 \theta \ll T \ll \theta \sqrt{\frac{G}{E}} \quad (G \ll E) \quad (4.58)$$

where A and B are coefficients expressed in terms of the elastic moduli of the crystal and the "transverse rigidity" of the chains; $\eta^2 = G/E$ (G is the shear modulus and E is Young's modulus along the z axis).

For the heat capacity of structures with interacting layers Lifshitz derived the equations:

$$C = A_1 \left(\frac{T}{\theta} \right)^3 \quad \text{at} \quad T < \eta_1^2 \theta \quad (4.59)$$

$$C = B_1 \left(\frac{T}{\theta} \right)^2 \quad \text{at} \quad \eta_1^2 \theta \ll T \ll \theta \sqrt{\frac{G}{E_1}} \quad (4.60)$$

where A_1 and B_1 are coefficients which are functions of the elastic moduli of the crystal and of the "transverse rigidity" of the layers; $\eta_1^2 = G/E_1$ (G is the shear modulus and E_1 is Young's modulus in the plane of the layer).

Equations (4.54) through (4.60) clearly do not agree even qualitatively with the experimental values of heat capacity obtained for linear polymers.

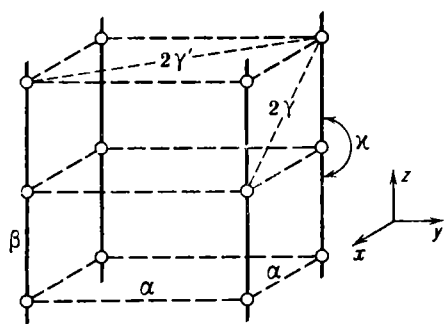


Fig. 4.1. The Hecht-Stockmayer model of a polymer crystal, taking into account various force constants. Polymeric chains are arranged along the z axis.

It should be noted that neither the Lifshitz nor the Tarasov theory takes into account many of the special features of polymers. The Hecht-Stockmayer theory (12) is to a considerable extent free from the shortcomings mentioned above.

4.1.2.3. The Hecht-Stockmayer Theory

Hecht and Stockmayer were the first to propose a simple model which enables one to calculate the vibrational spectrum of polymers with account taken of intermolecular interaction. For the purpose of calculations, Hecht and Stockmayer took a simple tetragonal lattice, which they used as a model of a polymeric crystal formed of chains arranged in parallel (Fig. 4.1). It was assumed that all the chain links have the same mass m and that the distance between the links is C along the chain and $a = b$ at right angles to the chain. The interaction between the chains was determined with the aid of the force constant α , which takes account of the interaction between the nearest neighbours in the x and y directions (at right angles to the chain axis) and also of the force constant β , which takes account of the interaction between neighbouring atoms (the valence forces) in the z direction (along the main chains). The interaction between other neighbouring links was described by introducing the force constants 2γ and $2\gamma'$, which take into account the influence of the links along the diagonal in the planes xz and yz (2γ) and also in the plane xy ($2\gamma'$) (see 4.1). Finally, the force constant κ takes account of the deformation of valence angles.

For numerical calculations Hecht and Stockmayer made use of the following reduced values of the dimensionless force constants: $\alpha_r = 0.03968$; $\beta_r = 0.992$; $\kappa_r = 0.0992$; $\gamma_r = \gamma'_r = 0.002$.

The ratio $\beta/\alpha = 25$ reflects the fact that the valence bonds play a substantially greater role than the bonds arising from the van der Waals forces operating between adjacent chains. The ratio $\kappa/\beta = 0.1$ is a good approximation for paraffins. For all the force constants used in the Hecht-Stockmayer model the inequality $\beta > \kappa > \alpha \gg \gamma = \gamma'$ holds true.

Hecht and Stockmayer (12) considered the equations of motion of a polymeric crystal, taking account of all the force constants given above. They arrived at an approximate solution of the secular equation for a simple lattice and showed that there correspond to this equation three acoustical branches, two of which coincide (they degenerate). The branches that degenerate characterize the natural vibrations at which the chain links are displaced perpendicular to the direction of the chain (deformation vibrations). The third acoustical branch defines natural vibrations at which the links are displaced along the chain (valence vibrations). Hecht and Stockmayer deduced an expression for the distribution function of natural vibrational frequencies and examined the manner in which it changes in the limiting case of low temperatures.

For heat capacity at constant volume these authors obtained the following expression:

$$C_v = 3R \int_{\nu=0}^{\nu=1} f(x) dI(\nu) \quad (4.61)$$

where $f(x) = x^2 e^x / (e^x - 1)^2$; $x = (T_m/T)_\nu$ (T_m is the characteristic temperature, $T_m = h\nu_m/k$); $I(\nu)$ is the reduced integral distribution function of normal vibration frequencies.

To calculate heat capacity using Eq. (4.61) it is necessary to perform a graphical integration of this equation. Such calculations have been carried out by Hecht and Stockmayer, who tabulated values of $C_v/3R$ as a function of the parameters T/T_m and θ_D/T . From Eq. (4.61) we see that the dependence $C_v \propto T^3$ will hold true only in a very narrow temperature range near 0 K. At higher temperatures C_v is proportional to T^2 . According to the Hecht-Stockmayer theory, the dependence $C_v \propto T^2$ is possible not only for lamellar structures.

The model proposed by Hecht and Stockmayer is a highly simplified model which by no means reflects fully the structure of a real polymer. Nonetheless it takes into account two most important features of polymers: the anisotropy of polymeric chains, which is defined by the inequality $\beta/\alpha \gg 1$, and chain flexibility, which is represented by the force constant κ . It should be noted that the Hecht-Stockmayer model can be used for quantitative calculations only when the chains of a polymer are straightened out. If the structure of a polymer is such that its chains form many gauche conformations or are helices (these two cases are most frequently encountered), the theory does not fit heat capacity values arrived at through experiment.

4.1.3. The Heat Capacity of Crystalline and Amorphous Polymers

The thermal characteristics of polymers, unlike those of low-molecular-mass substances, have been little studied. 6

The majority of experimental data on specific heat capacity refer to a temperature range, the lower limit of which corresponds to the temperature of liquid hydrogen (about 20 K) and the upper limit to the melting temperature. This temperature range turns out to be sufficient for the calculation of the main thermodynamic parameters of polymers (enthalpy, entropy) from the measured values of specific heat capacity. These are of great technical value. Of importance for the elucidation of the mechanism of the heat capacity of polymers are measurements carried out at lower temperatures. The measurement of the heat capacity of polymers in the temperature range from 1 to 20 K is of greatest interest for the comparison of experimental evidence with results of theoretical calculations and also for the elucidation of those specific features of polymers which distinguish them from low-molecular solids. Attempts to extrapolate the values of specific heat capacity of polymers measured at 20 K to lower temperatures do not, as a rule, lead to consistent results.

The comparatively small amount of experimental data on the specific heat capacity of polymers is also due to the considerable difficulties that arise in a theoretical interpretation of the results obtained. Indeed, at a first approximation it can be assumed (4) that the heat capacity of polymers in the solid state is given by

$$C = C_1 + C_2 + C_3 \quad (4.62)$$

where C_1 is the heat capacity due to lattice vibrations (this contribution to heat capacity is greatest at low temperatures); C_2 is the heat capacity due to characteristic vibrations, including the independent motion of individual groups in the repeating unit of the polymer; C_3 is the heat capacity due to the presence of defects.

The elucidation of the role of these contributions to the heat capacity of polymers even in the region of low temperatures, where the situation is substantially simplified, presents considerable difficulties. In this connection, the use of sophisticated models, such as the Hecht-Stockmayer model (12), are hardly of great interest, considering the scarcity of experimental data. More important at present is the comparison of experimental values of the heat capacity of polymers with the simplest, though rather approximate, models, such as the Debye and Tarasov models. In this connection, one of the tasks is to establish the limits of applicability of the Debye theory to polymers. At first glance, the use of the Debye theory for describing the behaviour of the heat capacity of polymers seems to be

unjustified since this theory does not take into account the main feature of polymeric chains—their one-dimensional structure. In actual fact, during the propagation of long Debye waves (when low-frequency vibrations are excited) polymeric chains interact with one another as a result of the presence of the intermolecular forces. As a result, in the polymer there arise three-dimensional vibrations, which are described by the Debye theory.

In the case of the propagation of short Debye waves the principal role in the spectrum is played by the vibrations directed along the skeleton of the polymeric chain. Obviously, it is in this case that the one-dimensional nature of the polymeric chain is manifested. The simplest continuum model, which takes into account both the three- and one-dimensional nature of the polymer, is the Tarasov model.

Nevertheless, neither the Debye nor the Tarasov model can provide an exact picture of the behaviour of the heat capacity of polymers since they ignore the dispersion of Debye waves. From the Debye theory it follows that the dependence $C \propto T^3$ must be observed at $T < \theta_D/12$; because of dispersion, however, this dependence is observed at $T < \theta_D/50$ or at still lower temperatures. It should be noted that the presence of dispersion may greatly distort the form of the dependence of heat capacity on temperature. Thus, while the Debye theory predicts that $C/T^3 = \text{constant}$, the presence of dispersion must lead to an increase in the quantity C/T^3 with temperature. According to the Tarasov theory (for a one-dimensional and a two-dimensional continuum) the quantity C/T^3 must decrease with rise of temperature. In the case of dispersion the quantity C/T^3 can remain constant even at relatively high temperatures.

Thus, the analysis of the temperature dependence of heat capacity gives one access to important information on the nature of polymers and the methodology of a theoretical description of this class of substances.

The temperature dependence of the heat capacity of polymers shows some specificity. It is essential that the heat capacities of amorphous and crystalline polymers differ considerably. The heat capacity of amorphous polymers is, as a rule, higher than the heat capacity of partly crystalline (especially, strongly crystallized) polymers. It would be of interest to find out how the heat capacity of a polymer is changed when its degree of crystallinity is altered. However, the only crystalline polymer that has been studied to a sufficient extent is polyethylene.

A special feature of linear polymers is that the heat capacity C_p is practically linearly dependent on temperature, at least in the temperature range from 20 K to T_g .

We shall see below that the differences in the temperature dependence of the heat capacity of amorphous and crystalline polymers are not accidental. Typical in this respect is polyethylene.

4.1.3.1. The Heat Capacity of Crystalline Polymers

Polyethylene is the most convenient subject for the study of heat capacity: it has a simple chemical structure and there are no bulky side groups, the motion of which can make a considerable contribution to heat capacity.

In order to compare the available experimental data with the results of theoretical calculations one must know the molar heat capacity of the polymer. By the molar heat capacity of a polymer is meant the heat capacity per 1 mole of the repeating unit. It is usually believed that in a polymer having a structure of type (A) the gram-mole is the molecular mass of the group (A) expressed in grams, while in polymers with a structure of type (AB) it is the molecular mass of the group (AB) expressed in grams. The correctness of this definition is confirmed by the fact that at high temperatures the Dulong-Petit law holds true: for substances of type (A) the heat capacity C at high temperatures tends to $0.025 \text{ kJ}/(\text{mole} \cdot \text{K})$ and for polymers of type (AB) it tends to $0.050 \text{ kJ}/(\text{mole} \cdot \text{K})$.

Since the repeating unit of polyethylene is the methylene group CH_2 , it is natural that all data on the molar heat capacity of this polymer refer to the mass $m = 14.03 \text{ g}$. Polyethylene is a partly crystalline polymer which forms an orthorhombic cell upon crystallization. The density of completely crystalline polyethylene is $\rho_{\text{cr}} = 0.999 \text{ Mg}/\text{m}^3$ and that of completely amorphous polyethylene is $\rho_{\text{am}} = 0.8525 \text{ Mg}/\text{m}^3$.

A detailed analysis of the available literature data on the heat capacity of polyethylene has been carried out by Wunderlich (4). This author has systematized the experimental values of C_p for polyethylene at temperatures from 1 to 420 K and calculated the enthalpy and entropy of the polymer; he has also calculated C_p for completely amorphous and completely crystalline samples. It was found that from 1 to 100 K the specific heat C_p of amorphous and completely crystalline samples of polyethylene is practically the same and only at $T > 100 \text{ K}$ does the specific heat of the amorphous sample begin to exceed the C_p value of the crystalline sample. From the experimental data reported by Wunderlich (4) it follows that at temperatures from 1 to 5 K the heat capacity of polyethylene strictly follows Debye's cube law. The Debye characteristic temperature calculated from experimental values of heat capacity is $\theta_D = 231 \text{ K}$.

It seems strange that the specific heat of polyethylene in the helium-temperature region does not depend on the degree of crystallinity. It was shown later (13) that the heat capacity of polyethylene depends on crystallinity not only in the region of relatively high temperatures (above 110 K) but also in the helium region. Figure 4.2 shows the temperature dependence of the specific heat capacity of

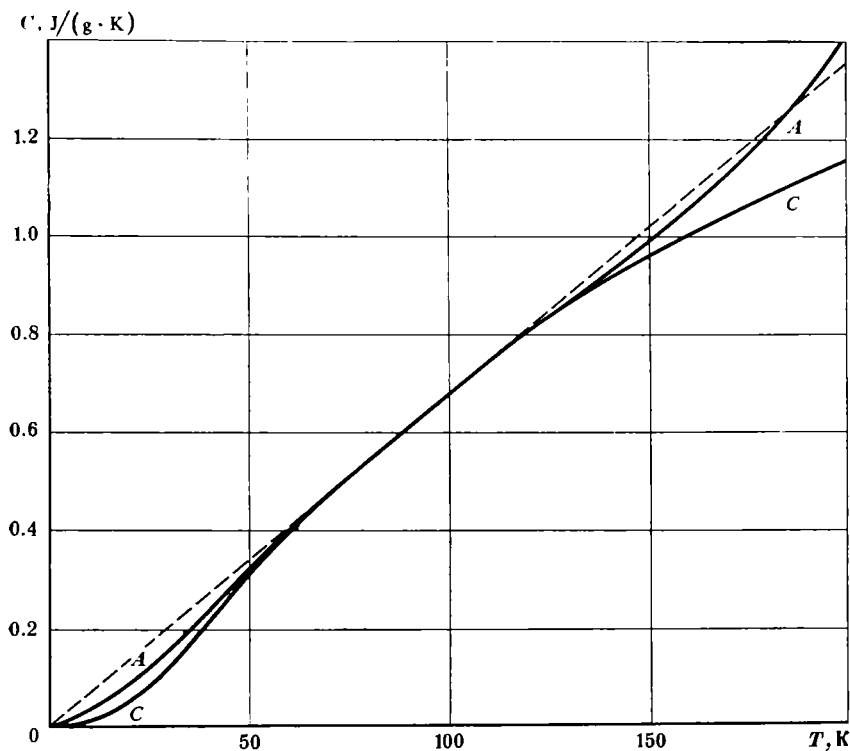


Fig. 4.2. The heat capacity of a completely crystalline (*C*) and amorphous (*A*) polyethylene (the results have been obtained by extrapolation to crystallinity values equal to 100 and 0 per cent). The dashed line is a continuation of the linear dependence of heat capacity, which is valid for the temperature range from 50 to 100 K.

completely amorphous and completely crystalline polyethylene. The values of C_p were obtained by extrapolation of experimental data on specific heat to $\alpha = 0$ (amorphous polyethylene) and to $\alpha = 1$ (crystalline polyethylene). From Fig. 4.2 it is seen that in the region of low (1-50 K) and of relatively high (110 K and higher) temperatures the heat capacities of amorphous and crystalline polyethylene are different. In both temperature ranges the heat capacity of amorphous polyethylene exceeds the corresponding values for crystalline polyethylene. The temperature range from 50 to 100 K is characteristic. Here the heat capacities of amorphous and crystalline polyethylene coincide and, what is more interesting, depend linearly on temperature, as predicted by the Tarasov theory. Moreover, the curves of $C_p = f(T)$ have the same slope in this region, which indicates that the characteristic temperature θ_1 in the Tarasov theory is independent of the density of polyethylene. This fact is an indication that in this temperature region there predominate in the vibrational spectrum of polyethylene one-dimensional vibrations, which at a first approxi-

mation are independent of the forces of interchain interaction (and, hence, of the density of the polymer) and are determined purely by the forces of intrachain interaction.

From Fig. 4.2 it can be seen that there exist two regions in which the heat capacities of amorphous and crystalline polyethylene differ. The high-temperature end of the $C_p = f(T)$ curve is associated with the transition of the amorphous regions of polyethylene from the glassy to the high-elastic (rubbery) state.

The dependence of C_p on the degree of crystallinity below 50 K is due to two factors: (1) in this region a considerable contribution to the acoustic spectrum of polyethylene is made by three-dimensional vibrations which are sensitive to the forces of interchain interaction and, hence, to the density of the polymer as well; (2) a considerable contribution can also be made by non-acoustic low-frequency vibrations which are caused by the presence of disordered amorphous regions.

In the temperature range 1-50 K the heat capacity of polyethylene is linearly dependent on the degree of crystallinity (9). This dependence is most strongly manifested at 5 K and becomes weaker with increase or decrease of temperature. Whereas the weakening of the dependence of C_p on the degree of crystallinity with rise of temperature from 5 to 50 K may be explained by an increase in the frequency of normal vibrations and by the subsequent transition to relatively high-frequency one-dimensional vibrations, the reason for the decrease of this dependence with fall of temperature below 5 K is not quite so clear. While the heat capacity of partly crystalline polyethylene obeys Debye's cube law only up to 5 K (13), the heat capacity of completely crystalline polyethylene obeys it up to 9 K. The characteristic temperature θ_D of fully crystalline polyethylene calculated by the Debye formula is found to be equal to 260 K.

For a hypothetically completely amorphous polyethylene sample the temperature dependence of heat capacity at temperatures from 0 to 6 K may be represented in the form:

$$C_{\text{am}} = 0.359 \times 10^{-3} T^3 + 45.45 \times 10^{-3} E(\theta_E/T) \text{ kJ/(kmole} \cdot \text{K)}$$

where $E(\theta_E/T)$ is the characteristic Einstein function with the Einstein characteristic temperature $\theta_E = 23^\circ\text{K}$.

For analysing the behaviour of heat capacity at low temperatures use is often made of the plot of C/T^3 against T . Figure 4.3 shows such a plot for completely amorphous and completely crystalline polyethylene. From this figure it can be seen that the quantity C/T^3 for crystalline polyethylene below 10 K is independent of temperature, whereas for amorphous polyethylene a "hump" near 5 K is observed. Thus, the temperature dependence of the heat capacity of amorphous polyethylene differs qualitatively from the same dependence for the fully crystalline polymer. The difference is that

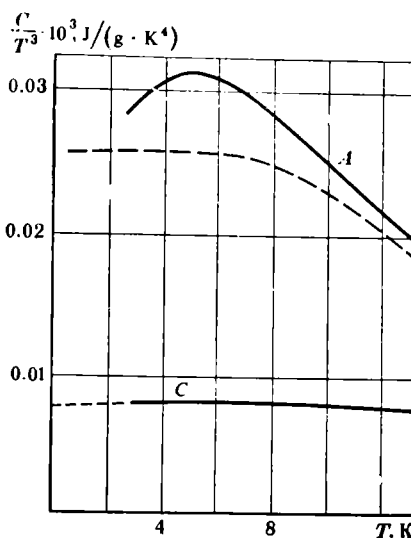


Fig. 4.3. The parameter C/T^3 versus temperature for completely crystalline (C) and completely amorphous (A) polyethylene. The dashed line represents data calculated according to the Tarasov theory.

even in the region of very low temperatures (1-5 K) the heat capacity of amorphous polyethylene cannot be fully described with the aid of the simple Debye formula. The heat capacity calculated from the Debye formula is only a part of the heat capacity of amorphous polyethylene at very low temperatures. The remaining, "excess", or "super-Debye" part of heat capacity can be described by using one or more characteristic Einstein functions. The "super-Debye" heat capacity at low temperatures is also a characteristic feature of other amorphous solids (14).

4.1.3.2. The Heat Capacity of Amorphous Polymers

The main feature of the heat capacity of amorphous polymers at low temperatures is the departure of its temperature dependence from Debye's cube law. Whereas for crystalline polymers at temperatures from 1 to 4 K the heat capacity obeys, as a rule, Debye's law, in the case of amorphous polymers there is observed, down to the lowest temperatures, a fundamental difference between the temperature dependence of heat capacity and the behaviour predicted by the Debye theory. This is manifested in that even at very low temperatures the relation $C/T^3 = \text{const}$, which follows from the Debye theory, does not hold for amorphous polymers. It has already been said that for completely amorphous polyethylene a hump is observed on the plot of $C/T^3 = f(T)$ near 5 K. The departure from the dependence $C/T^3 = \text{const}$ at low temperatures is a distinctive feature of many amorphous materials, both organic and inorganic.

A similar behaviour of heat capacity is observed with amorphous SiO_2 , GeO_2 , and selenium at $T < 1$ K. This effect is ascribed to the

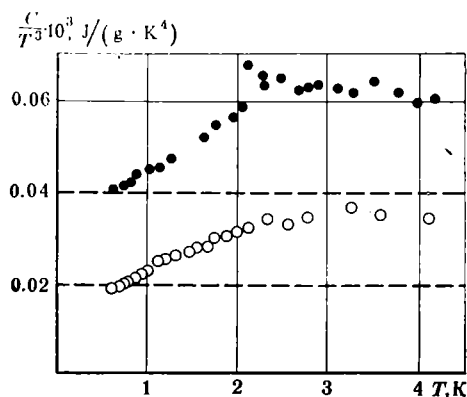


Fig. 4.4. The parameter C/T^3 versus temperature for polystyrene (●) and polymethyl methacrylate (○). The dashed lines represent the Debye contribution to the heat capacity.

presence of a small number of low-frequency optical vibrations due to the specificity of the amorphous state. For example, the heat capacity of completely amorphous polyethylene at low temperatures can be described by combining the frequency spectrum based on the Tarasov theory with a small number (0.17 per cent of repeating units) of vibrations with a characteristic temperature of 23 K.

Thus, typical of amorphous substances is the “super-Debye” or “excess” heat capacity. This contribution to heat capacity becomes especially noticeable if the Debye part, found from ultrasonic measurements extrapolated to 0 K is subtracted from the experimentally found values of heat capacity. The results of such calculations for polymethyl methacrylate and polystyrene are given in Fig. 4.4. From a comparison of the curves shown in Fig. 4.4 it becomes clear that, apart from the contribution of acoustic vibrations, the contribution from non-acoustic vibrations becomes substantial near the temperature of liquid helium. A remarkable feature is that the value of C/T^3 below 1.5 K falls off and tends to a limiting value predicted on the basis of ultrasonic measurements. This result should be treated cautiously since the values of the velocity of longitudinal and transverse waves are sometimes measured at temperatures $T > 120$ K and then extrapolated to 0 K. Nevertheless, for polymethyl methacrylate, just as for polystyrene, there clearly exists a non-acoustic, “super-Debye” contribution to heat capacity at helium temperatures.

A physical interpretation of the super-Debye contribution to low-temperature heat capacity is far from clear and can hardly be made on the basis of calorimetric measurements alone. General principles tell us that the excess heat capacity must be due to the small number of vibrations with discrete low frequencies. In amorphous SiO_2 , these vibrations are active in terms of Raman spectroscopy, which shows them as optical modes of vibration.

One possible physical interpretation is Rosenstock's idea (15) that low-frequency vibrational modes may be due to the presence of inner cavities or voids in the disordered structure. The vibrating kinetic units that are present inside or on the surface of these cavities are bound weakly with the lattice and therefore vibrate independently and with a low frequency. This model presupposes that the extra heat capacity can be detected in partly crystalline or completely amorphous polymers. Using the Rosenstock model, we can represent the heat capacity of an amorphous polymer as the sum of the Debye acoustic contribution and the super-Debye heat capacity due to independently vibrating oscillators. The frequency and the number of such oscillators can be found by using Einstein's theory of heat capacity. The nature of these oscillators has not yet been elucidated. Rees (13), for example, thinks that their role may be played by side groups. In the case of polymethyl methacrylate and amorphous polyethylene, methyl groups can play the role of oscillators (such groups in amorphous polyethylene play the role of branchings); as regards polystyrene, the situation is more complicated. The side groups in polystyrene are bulky phenyl groups which may be larger in size than the inner voids that are dealt with in the Rosenstock theory. A comparison of the characteristic frequencies shows that the mass of the vibrating kinetic unit of polystyrene is not much greater than in the case of polymethyl methacrylate and polyethylene. According to Rees, the role of Einstein oscillators in polystyrene can be played by the end groups or branchings.

Let us consider in more detail the low-temperature heat capacity of amorphous polymers. A typical amorphous polymer is polystyrene. The molar heat capacity of polystyrene is usually referred to 104.15 g of the polymer. Amorphous atactic polystyrene has been studied by many investigators (see, for example, 4, 14). The heat capacity of polystyrene has been measured at temperatures from 0.8 to 540 K. The most interesting result obtained from studies of polystyrene is that its heat capacity cannot be described with the aid of Debye's theory even at very low temperatures (about 1 K).

It has been shown (16) that the temperature dependence of the heat capacity of the polymer at very low temperatures can be depicted by combining Debye's formula at $\theta_D = 115$ K with two Einstein modes with the characteristic temperatures 5.5 and 16 K. The Einstein harmonic oscillators are, respectively, 0.038 and 1.8 per cent of the total number of oscillators. The question of the nature of the vibrating kinetic units, expressed in terms of the Einstein harmonic oscillators, remains open. One would think that these vibrations may be linked with the side groups, but in polystyrene these side groups are very bulky phenyl groups. The motion of these groups near the temperature of liquid helium is hardly probable.

One mechanism which might account for the Einstein contribution

to the heat capacity is as follows (17). Even amorphous polymers possess, to a certain extent, a one-dimensional order. Since the interaction between atoms in the chain (due to covalent bonds) is considerably stronger than the van der Waals interaction between chains, it has been supposed (17) that the units of isolated polymeric chains may be regarded as one-dimensional Einstein oscillators.

It has been found that the number of repeating units per one Einstein harmonic oscillator is 35-50, while one macromolecule of polystyrene contains 35-350 repeating units (depending on the molecular mass). This contradiction becomes understandable, however, if we take into account that the molecular mass of the portion of the polystyrene chain between neighbouring nodes of the space entanglement network is 33-45, according to the results of acoustic measurements (18).

It is customarily believed (13, 14) that the presence of excess super-Debye heat capacity at low temperatures, defined by the Einstein contribution to C_v , is a characteristic feature of amorphous substances, both organic and inorganic. It is supposed that this is associated with the presence of ordered regions in amorphous substances (these might be the units of the chain or small ordered but uncrystallized regions in amorphous polymers, or perhaps analogous regions in inorganic glasses). The vibrational spectrum of such ordered aggregates is discrete, and the lowest allowed frequency is excited at helium temperatures. This exerts a considerable effect on the low-temperature specific heat and thermal conductivity of such systems.

This point of view agrees well with the present-day conceptions of the supermolecular organization of amorphous polymers.

For more detailed information on the heat capacity of linear polymers, the reader is referred to the monographs of Wunderlich and Baur (4) and Godovsky (19).

4.2. Thermal Conductivity of Polymers

4.2.1. Basic Concepts of the Thermal Conductivity of Dielectrics

We understand by heat conduction in solids the heat flow from hotter regions of a solid to colder regions, as a result of which the temperatures become equalized. Let us consider a long thin rod. Suppose that the temperatures at the ends of this rod are T_1 and T_2 and the length of the rod is $l = x$; then a temperature gradient $\partial T / \partial x$ develops in the rod which results in the appearance of a heat flow along the rod.

The basic law of thermal conductivity is Fourier's law:

$$\bar{q} = -\kappa \text{ grad } T \quad (4.63)$$

where \bar{q} is the heat flux density vector (which is numerically equal to the energy transferred through the cross-sectional area of the specimen per unit time); κ is the thermal conductivity, usually in W/(m·K).

Heat conduction is an energy-transfer process. Like other energy-transfer processes, heat conduction is relaxational by its nature. Indeed, if the temperature in an element of a solid is changed in some way, the presence of a temperature gradient will lead to the generation of a heat flux which will exist until the temperature gradient becomes equal to zero as a result of the transfer of energy from sites with a higher temperature. If a constant temperature gradient is maintained artificially, a stationary, or steady-state, heat flux, constant in time, will develop in the solid.

According to the mechanism of heat transfer, all solids can be divided into three large groups: (1) nonmetals, in which the heat transfer takes place as a result of lattice vibrations; (2) metals, in which electrons play the principal role in heat conduction; (3) alloys and other poorly conducting substances, whose thermal conductivity is due to a combination of these two factors.

Let us consider the thermal conductivity of solids belonging to the first group, i.e., the thermal conductivity of dielectric materials, since the majority of polymeric materials are dielectrics. We shall first confine ourselves to a consideration of crystalline dielectrics. If the crystal lattice is regarded as a set of harmonic oscillators, in which the normal vibrations are independent of one another and the vibration amplitudes depend on temperature, then no thermal resistance will be present in such a lattice. Besides, because of the independence of the individual modes of vibrations and the absence of any interaction between them, the energy of each vibration remains unchanged and no equilibrium energy distribution can take place in such a system.

Debye made an attempt to take into account the interaction of lattice waves and employed the formula taken from the kinetic theory of gases for the determination of thermal conductivity:

$$\kappa = \frac{1}{3} C_v \bar{c} l \quad (4.64)$$

where C_v is the heat capacity per unit volume; \bar{c} is the average velocity of sound; l is the mean free path of phonons.

The quantity $\tau = l/\bar{c}$ represents the lifetime of the phonon.

At relatively high temperatures $C_v = \text{const}$ (as follows from the Dulong-Petit law) and the sound velocity in the Debye approximation is also taken to be practically independent of temperature, and therefore, since l is proportional to $1/T$, the thermal conductivity must be inversely proportional to the temperature T . As the temperature decreases the mean free path of phonons, l , increases and at sufficiently low temperatures l is determined by crystal size. Fur-

ther decreases in temperature no longer affect the value of l . In this region the thermal conductivity κ is proportional to C_v and, since at low temperatures C_v is proportional to T^3 , it follows that κ too depends on temperature according to the same law.

It has been shown that finite values of κ cannot be obtained from the theory of the elastic continuum. Thermal conductivity can be explained only by turning to dynamic lattice theory with account taken of anharmonicity phenomena.

According to the results obtained by Peierls (20), it follows from dynamic lattice theory that thermal conductivity depends on temperature in different ways in different temperature regions.

In the region of relatively high temperatures ($T \geq \theta_D$) the mean free path l is proportional to T^{-1} and κ is proportional to T^{-1} . At low temperatures, when $T \leq \theta_D$ the mean free path and thermal conductivity are both proportional to $e^{\theta_D/aT}$ (where a is a constant; according to Peierls, $a \approx 2$). In the region of very low temperatures (at $T \rightarrow 0$ K) $l = \text{const}$ and κ is proportional to T^3 . Such a dependence of thermal conductivity on temperature is in satisfactory agreement with experimental data.

The development of a rigorous theory of heat conduction, which would allow us to calculate thermal conductivity as a function of temperature, is one of the most important problems of solid-state physics; the construction of such a theory is beset by formidable mathematical difficulties. In solving this problem use is often made of assumptions, the correctness of which is not always obvious.

Here we shall limit ourselves to a qualitative consideration of the matter, enough to give one an insight into the mechanism of heat conduction in dielectrics at low temperatures.

The theory of heat conduction in dielectric crystals is developed in the following way. To describe the energy flux use is made of the concept of quasi-particles—phonons which are quantized thermal excitations of the lattice. It is assumed that in a periodic volume V , which contains N atoms, there exist $3N$ thermal vibrations, corresponding to the same number of waves. Each wave is characterized by the wave vector \vec{K} and three polarization vectors e_s . If the wave transfers an energy E_s^h , then its group velocity is given by

$$v_s^h = \frac{\partial \omega_s^h}{\partial K} \quad (4.65)$$

where ω_s^h is the circular frequency of the wave.

The density of the energy flux transferred by such a wave is defined by the relation:

$$q_s^h = \frac{E_s^h}{V} v_s^h \quad (4.66)$$

The density of the heat flux transferred within the crystal with the aid of all the lattice vibrations is deduced by summation of expression (4.66) over all the vibrations:

$$q = \frac{1}{V} \sum_{ks} E_s^k v_s^k \quad (4.67)$$

Usually, the energy values of individual waves satisfy a particular distribution of waves among the energies. In order to calculate the heat flux use has to be made of the concept of the average energy $\langle E_s^k \rangle = E(\omega_s^k, T)$.

In a quantum-mechanical treatment of lattice vibrations, instead of lattice waves one deals with phonons, characterized by the frequency ω_s^k , the pseudo-momentum $\hbar K$ and the polarization s . The lattice vibrations are taken as a phonon gas which obeys the Bose-Einstein statistics. The phonon gas is characterized by the distribution function \bar{N}_s^k which takes account of the number of particles in a given state. In this case, instead of the average energy $\langle E_s^k \rangle = E(\omega_s^k, T)$, use is made of the concept of average occupation numbers representing the distribution function \bar{N}_s^k .

In thermal equilibrium

$$(\bar{N}_s^k)_T = [e^{\hbar\omega_s^k/kT} - 1]^{-1} \quad (4.68)$$

In the case of steady-state heat conduction a temperature gradient leads to small departures from the average occupation numbers \bar{N}_s^k corresponding to the distribution in thermal equilibrium:

$$\bar{N}_s^k = (N_s^k)_T + n_s^k \quad (4.69)$$

where \bar{N}_s^k is the nonequilibrium distribution function; $(N_s^k)_T$ is the distribution function corresponding to the state of thermal equilibrium; n_s^k is a minor addition which takes account of the departure of the distribution function from the equilibrium value.

A contribution to the heat transfer and, hence, to the heat flux, is made only by the term n_s^k , which represents the departure from the thermal equilibrium.

The heat flux density in this case is given by

$$q = \frac{1}{V} \sum \hbar\omega_s^k n_s^k v_s^k \quad (4.70)$$

The main task is to determine the values of n_s^k ; they must be proportional to the temperature gradient. In this case, one can derive expressions for the thermal conductivity. To solve this problem, the Boltzmann kinetic equation is used.

The change in the distribution function $\left. \frac{d\bar{N}_s^k}{dt} \right|_1$ in the neighbourhood of a particular point caused by the external temperature field is compensated for by the collision of phonons with one another and also with other particles. Since in the steady state \bar{N}_s^k is constant in time, it follows that

$$\left. \frac{\partial \bar{N}_s^k}{\partial t} \right|_1 - \left. \frac{\partial \bar{N}_s^k}{\partial t} \right|_2 = 0 \quad (4.71)$$

in which expression the first term takes account of the variation of the distribution function due to the convection of phonons, and the second the change caused by the collision between phonons (also by the interaction between phonons and lattice defects).

Expression (4.71) is an integro-differential equation. Its form and structure depend on the type of phonon interaction and its solution is beset by considerable mathematical difficulties. There are various methods for solving it (21-23).

In solving the kinetic equation the Hamiltonian operator (or simply the Hamiltonian) H is written in the form

$$H = H_0 + \Phi_3 \quad (4.72)$$

where H_0 is the harmonic part of the Hamiltonian, which depends on the kinetic energy and the quadratic terms of the potential energy.

The potential energy of the lattice Φ , which is a function only of the coordinates of atomic nuclei and is a sum of the energy of Coulomb interaction between nuclei and electrons and the kinetic energy of electrons, can be expanded into a power series in the degrees of displacements of nuclei from the equilibrium position. In this case

$$\Phi = \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \dots \quad (4.73)$$

where the term Φ_0 is the potential energy of the crystal in the equilibrium state.

With an appropriate choice of the coordinate origin Φ_0 can be made equal to zero. If Φ is expanded into a series about the equilibrium position, the linear term Φ_1 also becomes zero. If we neglect the higher terms in the expansion and retain the quadratic (with respect to displacements from the equilibrium position) term Φ_2 , we obtain the so-called harmonic approximation. The coefficients in Φ_2 determine the forces that act on the structural units of the lattice for small departures from the equilibrium position. It is in the harmonic approximation precisely that the Debye theory of heat capacity is valid. In this approximation the heat capacity of the lattice cannot be explained.

With large departures of particles from their equilibrium positions (in cases of high elastic stresses or high temperatures) higher

(as compared with Φ_2) terms of the series must be taken into account in expression (4.73). If the terms Φ_3 and Φ_4 (or, at the very least, only Φ_3) are retained in expression (4.73), then we can describe the thermal conductivity of a dielectric crystal. It is exactly such anharmonic terms of the expansion (4.73) that are contained in the Hamiltonian (4.72) for the crystal lattice in calculations of thermal conductivity. The nonlinear anharmonic terms in the expansion of the potential energy determine the nature of the interaction of phonons. If the Hamiltonian (4.72) contains the term Φ_3 , it means that three-phonon processes are involved. An example of such a process is the interaction of two phonons with energies $\hbar\nu_1$ and $\hbar\nu_2$ and pseudo-momenta $\hbar K_1$ and $\hbar K_2$, in which these two phonons are annihilated and one with third phonon of energy $\hbar\nu$ and pseudo-momentum $\hbar K$ is created. A variant of three-phonon interaction, in which one phonon is split into two phonons, is also possible.

Two types of phonon processes are possible. In one of these, the interaction of phonons occurs in such a way that the pseudo-momentum of a system of interacting phonons is not changed. This case is described by the following relation between the wave vectors of the interacting phonons:

$$\bar{K}_1 + \bar{K}_2 + \bar{K} = 0 \quad (4.74)$$

Evidently, the total momentum of all phonons that arise in a dielectric crystal cannot change. Such phonon processes have come to be known as "Normal" or N-processes. "Normal" processes lead only to the redistribution of momentum and energy between the interacting phonons. Here the heat flux corresponding to the total pseudo-momentum of the phonons must not be attenuated. The additional factor responsible for this is that the heat transfer in a dielectric crystal is associated with the change in the number of phonons. When only the "Normal" processes are considered, the kinetic equation has no solution and the thermal resistance of crystals turns to zero. This is equivalent to the thermal conductivity becoming infinitely large. Hence, the "Normal" processes alone cannot lead to a finite value of the thermal conductivity of dielectrics.

In order to have thermal resistance, processes in which the total momentum of phonons is changed are required. If in a three-phonon interaction there is fulfilled the condition

$$\bar{K}_1 + \bar{K}_2 + \bar{K} = 2\pi\bar{b} \quad (4.75)$$

(where \bar{b} is one of the vectors of the reciprocal lattice), the total quasi-momentum of all the interacting phonons does not remain constant. The direction of the wave vectors in such an interaction is changed from what one would expect from the ordinary law of conservation of momentum. Therefore, the processes of phonon interaction, in which

the law of conservation of pseudo-momentum is not fulfilled, are known as "Umklapp" processes or U -processes. (We have already spoken about the pseudo-momentum of phonons.) This is associated with the fact that the quantity $\hbar K$ is not, strictly speaking, the momentum of lattice vibration. Therefore, strictly speaking, expressions (4.74) and (4.75) are not laws of conservation.

The mechanism of heat conduction in a dielectric crystal consists in that the long-wave phonons, whose energy is insufficient for the development of "Umklapp" processes, give rise, as the result of collisions ("Normal" processes), to nonequilibrium (excited) phonons of high energy. The collisions of such phonons occur, according to expression (4.75), with a change in the pseudo-momentum of the interacting phonons ("Umklapp" processes). The "Umklapp" processes lead to the appearance of a finite value of thermal conductivity and of a non-zero thermal resistance of dielectric crystals. It is primarily the "Umklapp" processes that govern the course of the temperature dependence of thermal conductivity. At very low temperatures (at $T \rightarrow 0$ K) the "Umklapp" processes are frozen, since the energy of nonequilibrium phonons is no longer sufficient for the occurrence of these processes. As the temperature mounts the "Umklapp" processes are unfrozen for those branches of the spectrum which first appear at the boundary of the Brillouin zone. Therefore, for transverse acoustic modes the "Umklapp" processes may occur at lower temperatures (22) than for longitudinal modes. This leads to an increase in the coefficient a in the expression for thermal conductivity ($\kappa \propto e^{\theta_D/aT}$) and to the narrowing of the range in which κ is exponentially dependent on temperature.

If the term Φ_4 in the expansion of the potential energy [formula (4.73)] is retained, this means that four-phonon processes must be considered.

The status of the theory of the thermal conductivity of dielectrics is such that one can only roughly estimate the nature of the temperature dependence of κ while taking account of the particular mechanisms of phonon processes.

For the ideal face-centred cubic lattice, Leibfried and Schloemann (24) deduced the following expression, using the variational method of solving the kinetic equation:

$$\kappa = \frac{3\sqrt[3]{4}}{10\pi^3} \frac{k^3}{\hbar^3} \frac{V_0^{1/3} M \theta_D^3}{\gamma^2 T} \quad (4.76)$$

where γ is the Grüneisen constant; V_0 is the atomic volume ($V_0 = V/N_0$); M is the mass.

Expression (4.76) is valid for relatively high temperatures ($T > \theta_D$). At lower temperatures ($T < \theta_D$), when heat conduction is governed by "Umklapp" processes, the thermal conductivity is

given by the relation:

$$\kappa \propto \left(\frac{\theta_D}{T} \right) e^{\theta_D/aT} \quad (4.77)$$

With further decrease of temperature, when the "Umklapp" processes are found to be frozen and the mean free path is considerably increased, the major role is played by the scattering of phonons at the boundaries of crystallites or at the external boundaries of the specimen. In this case the thermal conductivity is given by

$$\kappa = \frac{1}{3} C_v \bar{c} l = \frac{4\pi k^4 T^3}{h^3 \bar{c}^2} l \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (4.78)$$

where C_v is given by expression (4.18); $l = L\alpha^2$ (where L is the average distance between the boundaries of crystallites and α is a specific angle).

When phonons are scattered at the outer boundaries of crystallites the mean free path has the order of the smallest linear size of the specimen.

Apart from the "Umklapp" processes and phonon scattering, at the boundaries of crystallites (or at the outer boundaries of the specimen) there occur other types of phonon scattering as well, which lead to a finite thermal resistance.

Consideration of the thermal conductivity of amorphous solids presents considerable difficulties that arise out of the absence of translational symmetry in the arrangement of atoms, i.e., of the long-range order. By virtue of even this difference between amorphous solids and crystals the mechanism of heat transfer in amorphous solids might be expected to be different from that in crystals.

Indeed, the available experimental data indicate that the temperature dependence of thermal conductivity for amorphous solids is qualitatively different from the dependence of κ on T for crystalline solids. This becomes especially prominent if we compare the dependences $\kappa = f(T)$ for a substance which can be produced in both the amorphous and the crystalline state (Fig. 4.5).

In contrast to the thermal conductivity of crystalline bodies, the thermal conductivity of amorphous substances has no low-temperature maximum and, as a rule, it increases with rise of temperature. The slope of the $\kappa = f(T)$ curve may change in this case and at high temperatures the thermal conductivity tends to a constant limit. All this leads one to believe that a qualitatively different mechanism of heat conduction takes place in amorphous solids.

In dealing with the thermal conductivity of amorphous solids one often makes use of the Debye formula (4.64). The main task here is to determine the mean free path of phonons. By using the known experimental data one can occasionally estimate the magnitude of the

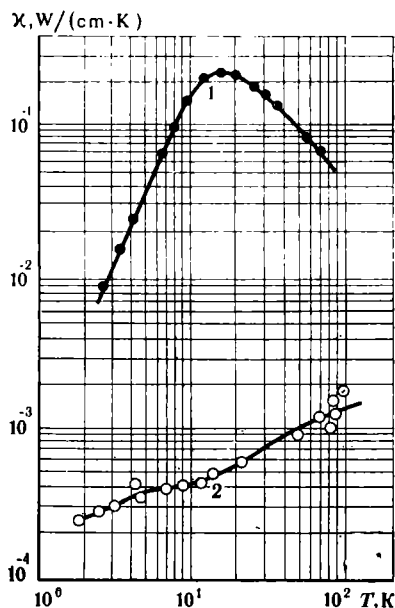


Fig. 4.5. Temperature dependence of the thermal conductivity coefficient of selenium:

1—crystalline sample; 2—amorphous sample.

mean free path l with the aid of formula (4.64). According to these estimates, the value of l is in good agreement with the sizes of the structural units in amorphous solids. For instance, Kittel (1) has shown that the mean free path in amorphous quartz glass is close to the sizes of the structural unit characteristic of this material. Indeed, the mean free path of phonons, l , in quartz glass at room temperature is equal to 8 \AA , whereas the dimensions of the tetrahedral cell of silicon dioxide are 7 \AA . Klemens, who analysed the temperature dependence of thermal conductivity, also came to the conclusion (21) that it is associated with the regions of short-range order in quartz glass.

The random, disordered arrangement of atoms in an amorphous solid is responsible for the fact that its elastic properties change from point to point. If an elastic wave propagates in such a solid, it may, in certain cases, undergo scattering, just as is the case in a medium with random inhomogeneities. Hence, the scattering of phonons may be expected to result from the change in their velocity from one point of the amorphous solid to another.

Employing a mathematical apparatus analogous to the one used for describing the propagation of radio waves in an irregularly refracting medium, Ziman examined the problem of the scattering of Debye elastic waves in an amorphous substance (33, 36). The line of his reasoning is as follows. Suppose that a plane monochromatic wave strikes a layer of an amorphous substance which is a disordered medium of thickness x_0 . Having passed through the layer of thickness

x , the wave on the surface of the layer will be characterized by a random distribution of phases. Assuming that to each point of the layer there corresponds a definite local velocity of elastic waves, c , which differs from the average velocity c_0 by an amount δc , we can calculate the mean square of the phase shift on the layer surface. The change of the phase $d\varphi$ of the wave that has travelled the path dx may be represented in the form

$$d\varphi = \frac{2\pi}{\lambda} \cdot \frac{\delta c}{c_0} dx \quad (4.79)$$

where λ is the wavelength of the propagating wave.

Further, a very important assumption is made that the quantity δc is not entirely accidental and near each point of the layer there is a small distance L over which δc changes but only slightly. The parameter L has come to be called the correlation length. It must be of the same order of magnitude as the average size of the structural unit of the amorphous solid. Thus, the correlation length may be compared with the sizes of the regions in which a short-range order is retained. Ziman postulated that the correlation function of the values of δc at points a distance R apart has the following form:

$$\frac{\delta c(r+R) \delta c(r)}{\langle \delta c \rangle^2} = e^{-R^2/L^2} \quad (4.80)$$

Further it is necessary to calculate the mean square of the phase shift $\langle \varphi^2 \rangle$ on the layer surface that has been crossed by the wave:

$$\langle \varphi^2 \rangle = 4\pi^{5/2} \frac{L \langle \delta c \rangle^2}{\lambda^2 c_0^2} x_0 \quad (4.81)$$

If the length of the propagating wave $\lambda \gg L$, then the expression for the mean free path may be written in the form:

$$l_1 = \frac{x_0}{\pi \langle \varphi^2 \rangle} = \frac{1}{4} \pi^{-7/2} \frac{c_0^2 \lambda^2}{\langle \delta c \rangle^2} L \quad (4.82)$$

If $\lambda \ll L$, then the mean free path is given by

$$l_2 = \pi^{-5/2} \frac{c_0^2}{\langle \delta c \rangle^2} L \quad (4.83)$$

From formulas (4.82) and (4.83) it follows that in the case of long waves, when the wavelength λ is much larger than the length of elastic correlation,¹ the mean free path l is proportional to λ^2 . In a case where $\lambda \ll L$, the mean free path is independent of the wavelength and is a constant quantity. In this case, inside the correlation region of L the wave propagates without being scattered, but it is strongly refracted at the boundaries of the region.

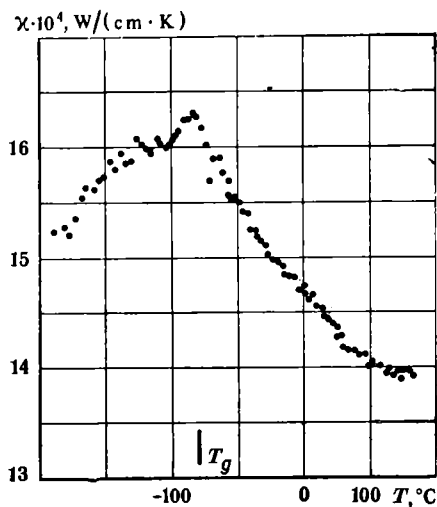


Fig. 4.6. Temperature dependence of the thermal conductivity coefficient of natural rubber.

4.2.2. Theories of the Thermal Conductivity of Polymers

The main emphasis in numerous investigations of thermal conductivity has been placed on the temperature range close to room temperature. The purpose of the majority of investigations was to establish the dependence of thermal conductivity on structure, chemical constitution, and temperature. The most important point here is a substantial difference in thermal conductivity between amorphous and crystalline polymers.

A typical feature of amorphous polymers is that up to the glass-transition temperature (T_g) thermal conductivity increases with rise of temperature and above T_g it begins to decrease (Fig. 4.6). An analogous fall in thermal conductivity above T_g has been observed for a number of amorphous polymers: natural rubber, polyisobutylene, polyvinyl chloride, atactic polypropylene, polymethyl methacrylate (19, 25-28). Eierman (26, 27) made an attempt to explain this phenomenon, using conceptual models which, in his opinion, could be applied to all amorphous materials.

4.2.2.1. The Eierman Theory

Eierman assumed that in an amorphous substance each bond between neighbouring atoms is equivalent to thermal resistance and calculated such an elementary thermal resistance r_e . The thermal resistance of a macroscopic amorphous sample is, according to Eierman, a network of elementary thermal resistances with atoms situated at the entanglement points. The elementary thermal resistance depends on the bonding forces operating between atoms. It decreases with increases in the elastic constant k_b , which characterizes the

bond. Therefore, the principal-valency chain of the polymer has a considerably lower thermal resistance than the van der Waals bonds. According to Eierman,

$$r_e = \frac{1}{\text{const} \cdot C_A} \sqrt{\frac{m_A}{k_b}} \quad (4.84)$$

where m_A is the mean arithmetic mass of two adjacent atoms; C_A is the heat capacity per atom; the constant is approximately equal to unity.

Eierman's reasoning is based on the well-known Debye formula for the determination of thermal conductivity:

$$\kappa = \Lambda \rho C \bar{l} \quad (4.85)$$

where Λ is a constant close to unity.

Further it is assumed that

$$\kappa = \Lambda \rho \sum_i C_i \bar{c}_i l_i \quad (4.86)$$

The subscript i refers to an individual wave from the vibrational spectrum. Assuming that the mean free path in amorphous substances coincides, at a first approximation, with the mean distance between two neighbouring atoms ($l \approx d$), Eierman writes the elementary thermal resistance in the form:

$$r_e = \frac{1}{\kappa_e} \cdot \frac{d}{ab} \quad (4.87)$$

where κ_e is the elementary thermal conductivity calculated from formula (4.85); the quantities a and b characterize the cross-sectional area of the volume element.

The velocity of sound in a chain of atoms in calculations of thermal resistance in the principal-valency chain is determined by the formula:

$$c = d \sqrt{k_b/m} \quad (4.88)$$

where k_b is the elastic constant which characterizes the bonding force between two neighbouring atoms with masses m_1 and m_2 ; $m = 0.5 (m_1 + m_2)$.

Formula (4.88) describes the propagation of a longitudinal wave in a chain of atoms. An analogous expression is written for a transverse wave. For the density of the volume element use is made of the formula $\rho_e = m/abd$ (26). Such a consideration leads to the expression for the elementary thermal resistance (4.84). For the elementary thermal conductivity the following formula obtains:

$$\kappa_e = \Lambda \frac{C_A d}{ab} \sqrt{\frac{k_b}{m}} \quad (4.89)$$

The thermal resistance due to the van der Waals interaction between adjacent chains is much greater than r_e in the primary-valence chain. To calculate the elementary thermal resistance due to the van der Waals forces, it is necessary to determine the corresponding elastic constants. They are found by using the intermolecular interaction potential in the form

$$\Phi = -2\varepsilon \left(\frac{r_{\min}}{r} \right)^6 + \varepsilon \left(\frac{r_{\min}}{r} \right)^{12} \quad (4.90)$$

where r is the distance between the interacting atoms situated in neighbouring polymeric chains; r_{\min} is the distance between the same atoms, corresponding to the minimum of the potential energy.

The Eierman theory makes it possible to account for the fall of thermal conductivity in amorphous polymers above T_g . We know that in amorphous polymers above T_g the thermal expansion is substantially increased, as a result of which the free volume increases. This leads to an increase in the mean distance between neighbouring chains and, hence, to a decrease in the elastic constants caused by the intermolecular interaction. As a result, thermal resistance is increased and, hence, thermal conductivity decreases. Since the thermal conductivity of amorphous polymers depends first of all on the van der Waals bonds, the change in the temperature coefficient of thermal conductivity is intimately connected with the change in the cubic expansion coefficient at T_g (26):

$$\Delta \left(\frac{1}{\kappa} \cdot \frac{d\kappa}{dT} \right) = -5.8\Delta\beta \quad (4.91)$$

where $(1/\kappa) \cdot (d\kappa/dT)$ is the temperature coefficient of thermal conductivity; β is the cubic expansion coefficient. Relation (4.91) holds true for various amorphous polymers and is independent of temperature.

In oriented amorphous polymers, the heat conduction in the direction of the orientation axis is substantially greater than in the perpendicular direction. The Eierman theory (26-28) provides an explanation for this phenomenon. When polymeric chains are being oriented, the primary valence bonds, which have a low thermal resistance, are arranged along the direction of orientation, and the van der Waals bonds, which have a high thermal resistance, are arranged at right angles to it. The model proposed by Eierman (26, 27) yields the following relation:

$$\frac{1}{\kappa_{\parallel}} + \frac{2}{\kappa_{\perp}} = \frac{3}{\kappa_0} \quad (4.92)$$

where κ_{\parallel} is the thermal conductivity of the polymer along the orientation axis; κ_{\perp} is the thermal conductivity of the same polymer, measured at right angles to the direction of orientation; κ_0 is the thermal

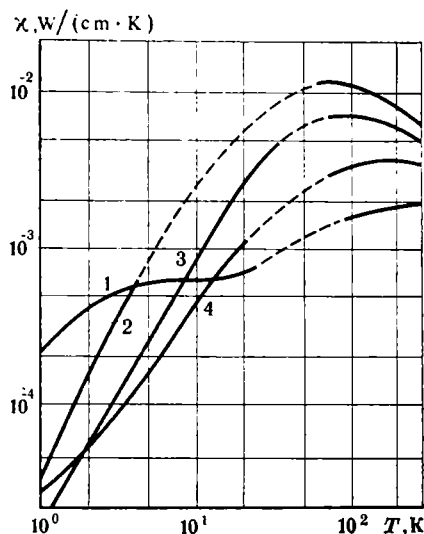


Fig. 4.7. Temperature dependence of the thermal conductivity coefficients of amorphous and crystalline polymers at low temperatures:

1— polymethyl methacrylate; 2, 3, 4 — polyethylene with densities 0.98, 0.96, and 0.92, respectively.

conductivity of an isotropic sample of the same polymer. This equation works well for polymethyl methacrylate and some other polymers near room temperature.

Crystalline polymers can be divided into two groups according to the temperature dependence of thermal conductivity. In the first group we find polyethylene and polyformaldehyde, whose thermal conductivities decrease with increasing temperature. The second group includes all other crystalline polymers (polyethylene terephthalate, isotactic polypropylene, polytrifluorochloroethylene, polytetrafluoroethylene, etc.), whose thermal conductivities increase with rise of temperature. The temperature dependence of the thermal conductivity of crystalline polymers belonging to the second group is analogous to that for amorphous polymers. The magnitude of thermal conductivity is appreciably affected by the degree of crystallinity of the polymer. This influence is especially pronounced at low temperatures.

The temperature dependences of the thermal conductivities of amorphous and crystalline polymers at low temperatures are fundamentally different. The temperature dependence of the κ of crystalline polymers is similar to the analogous dependence of imperfect crystals. On the curve of κ versus T we observe a maximum near 100 K, which shifts to low temperatures with increasing degree of crystallinity. The height of the maximum increases in this case (Fig. 4.7).

The temperature dependence of the thermal conductivity of amorphous polymers is similar to that of glass; it has no low-temperature maximum, but in the range 5–15 K a plateau appears (see Fig. 4.7). Above and below this region the thermal conductivity increases.

with rise of temperature. We have said above that the thermal conductivity of polymers depends significantly on the orientation. In the region of helium temperatures, however, the orientation either has no effect at all or exerts a very slight influence on the thermal conductivity of amorphous polymers.

Theories that explain the thermal conductivity of polymers can be classified into two groups: (1) theories which rely on the theory of the liquid state (25-28) and treat the transfer of energy between the repeating units via chemical bonds (primary or secondary) as an individual uncorrelated phenomenon; (2) theories which make use of the concepts of solid-state theory and deal with the cooperative motion of repeating units and the phenomena of phonon scattering which limit the region of energies of transfer. At low temperatures, when vibrations are excited with a wavelength much greater than the distances between the repeating units, naturally theories of the second type are resorted to.

In the case of amorphous polymers at high temperatures, when the mean free path is of the same order of magnitude as the distance between the repeating units, the theories of the second type in application hardly differ from the theory of the liquid state. The criterion for the applicability of theories of the second type to the problems of heat conduction in polymers is as follows: the mean free path must be much greater than the distance between particles. Obviously, only in such a case can one speak of cooperative vibrations. In describing the behaviour of the thermal conductivity of polymers in the low-temperature region, mostly theories of the second type are used. Energy transfer in polymers is ordinarily described with the aid of the Debye formula, which, according to Klemens (29), can be written in the form:

$$\kappa = \alpha C_p c l \quad (4.93)$$

where $\alpha = \cos^2\theta$ (θ is the angle between the direction of the path of phonons and the direction of energy transfer); with the exception of oriented polymers, $\alpha = 1/3$.

The main difficulty here lies in the calculation of the mean free path. There exist two types of phenomena which determine the magnitude of the mean free path: the interaction between phonons and the interaction of phonons with defects. For amorphous-crystalline polymers the phonon-phonon interaction is probably the prevailing mechanism at relatively high temperatures. As a consequence, κ is proportional to $1/T$. If the thermal resistance of polymers were caused only by "Umklapp" processes, which can occur at $T < \theta_D$, then in this case at low temperatures the thermal conductivity would be proportional to $\exp(1/T)$.

In the presence of defects the mean free path l decreases. Thermal conductivity is simultaneously reduced. Different types of defects

necessarily give rise to different types of temperature dependence of κ . Strictly speaking, these arguments apply to crystalline solids, whose thermal conductivity increases with fall of temperature, passes through a maximum and then decreases again. The temperature of the maximum usually decreases as the number of defects is reduced. Any attempt to extend the model based on lattice vibrations to the case of non-crystalline solids is unrealistic since in such solids there is no translational symmetry and no "Umklapp" processes can occur in them.

4.2.2.2. Structural Scattering

One of the first attempts to extend the conceptions that are valid for crystalline solids to amorphous substances was undertaken by Klemens (29). He assumed that the "elastic" disorder in the structure of glassy substances can be responsible for the scattering of phonons at any temperature. Klemens coined the term "structural scattering" for processes of this kind. The most important criterion for structural scattering is the ratio of the wavelength of the phonon to the length of elastic correlation. When the wavelength of the phonon and the elastic correlation length are of the same order of magnitude, the scattering is most intensive and the mean free path will be of the same order as the length of elastic correlation. If the wavelength of the phonon is much larger than the length of elastic correlation, the resulting distortion of the wavefront is not great and the difference between the successive wavefronts is smaller than the difference between the sites of elastic disorder.

Klemens assumed that in the case of long waves the mean free path of the phonon, l , is connected with its wave vector \bar{K} by the following relation:

$$l = A/(aK^2) \quad (4.94)$$

where A is a constant characterizing the length of elastic correlation; a is the distance between oscillating units.

In this case at low temperatures thermal conductivity is found to be proportional to the absolute temperature.

The theory of structural scattering predicts that for short waves l is proportional to Aa and for long waves l is proportional to $1/K^2$. While examining the question of the nature of the plateau in the temperature dependence of thermal conductivity for silicate glasses, Klemens had to assume (30) that the parameter A for longitudinal waves is much larger than for transverse waves. In fact, this hypothesis is based on the assumption that in a glassy material the change of the velocity, δc_T , of transverse waves is considerably greater than that of the velocity, δc_L , of longitudinal waves. From this hypothesis it follows that the main contribution to the low-temperature ther-

mal conductivity comes from longitudinal waves. A more detailed analysis led Klemens to a conclusion on the manner in which the predominant effect of longitudinal phonons on thermal conductivity is realized. As a result of the interaction, longitudinal phonons are converted into transverse phonons, which are intensively scattered. The transformation of longitudinal into transverse waves limits the mean free path and leads to the appearance of a low-temperature plateau in the temperature dependence of thermal conductivity. In order to account for this process, Klemens formulated thermal conductivity as follows:

$$\kappa = \kappa_L + \kappa_T \quad (4.95)$$

where κ_L is the contribution of longitudinal waves to thermal conductivity and κ_T is the contribution made by transverse waves.

The expression for κ_L takes the form:

$$\kappa_L = \frac{k_0^2}{3\pi h} \cdot \frac{A}{a} T y^2 \int_0^\infty \frac{e^x}{(e^x - 1)^2 x^2} \cdot \frac{x^2}{x^2 + y^2} dx \quad (4.96)$$

where k_0 is the Boltzmann constant; h is Planck's constant; the dimensionless parameter $y^2 = (T_0/T)^2$; $x = h\nu/(k_0T)$; T_0 is the parameter which has the dimensions of temperature and characterizes the process of transformation of longitudinal into transverse phonons.

The expression for κ_T has the form

$$\kappa_T = \frac{1}{3} v_T C l_T \quad (4.97)$$

where v_T is the group velocity of transverse phonons; l_T is the mean free path of transverse phonons ($l_T = A_T a$).

Rees (31) modified the Klemens theory, assuming that expression (4.97) can be represented as the sum of two terms, just as in the Tarasov model of the heat capacity of polymers. Then, the part of the thermal conductivity in expression (4.97) due to three-dimensional lattice vibrations is given by

$$\kappa_3 = \frac{1}{3} v_T C_3 l_T \quad (4.98)$$

where C_3 is the part of heat capacity due to three-dimensional vibrations.

The part of thermal conductivity that is associated with one-dimensional vibrations is defined as

$$\kappa_1 = \alpha v_1 C_1 l_1 \quad (4.99)$$

where α is a whole number accounting for the orientation of chains; v_1 is the velocity of propagation of one-dimensional vibrations, which can be determined if the characteristic temperature θ_1 is known.

Taking cognizance of expressions (4.97) through (4.99), we can write formula (4.95) as follows:

$$\kappa = \kappa_L + \frac{1}{3} v_T C_3 l_T + \alpha v_1 C_1 l_1 \quad (4.100)$$

The use of formula (4.100) enabled Rees to describe satisfactorily the thermal conductivity of some amorphous polymers at low temperatures.

4.2.2.3. *The Thermal Conductivity of Crystalline and Amorphous Polymers*

One of the parameters that have an appreciable effect on the magnitude and mode of variation of thermal conductivity at low temperatures is the degree of crystallinity λ . The thermal conductivity of a partly crystalline polymer is usually treated as a certain combination of the thermal conductivities of completely amorphous and completely crystalline samples of the same polymer. It is believed that the thermal conductivity of a partly crystalline polymer can be represented as follows:

$$\kappa = \lambda \kappa_{cr} + (1 - \lambda) \kappa_{am} \quad (4.101)$$

where λ is the degree of crystallinity; κ_{cr} and κ_{am} are the thermal conductivities of a completely crystalline and a completely amorphous sample of the same polymer.

In order to take account of the effect of the degree of crystallinity on thermal conductivity, Eierman (26, 27) made use of the formula derived by Maxwell for the electrical conductivity of a mixture consisting of spherical particles uniformly distributed in a homogeneous continuous medium:

$$\kappa = \frac{2\kappa_{am} + \kappa_{cr} + 2\lambda(\kappa_{cr} - \kappa_{am})}{2\kappa_{am} + \kappa_{cr} - \lambda(\kappa_{cr} - \kappa_{am})} \quad (4.102)$$

Using formula (4.101) or (4.102), one can pick out the thermal conductivity of the "amorphous" and "completely crystalline" parts of the polymer. Calculations of this kind should be carried out very cautiously because the parameters κ_{cr} and κ_{am} vary strongly with change of temperature over a wide range. In such a case, the densities of amorphous and crystalline samples are also greatly altered. Formulas (4.101) and (4.102) contain, as a rule, the values of crystallinity λ calculated from the measurements of ρ_{cr} and ρ_{am} at room temperature. The question of using formula (4.102) is highly problematic since it is valid only in those cases where the crystalline regions are uniformly distributed as inclusions in the amorphous matrix. In dealing with highly crystalline polymers, say, polyethylene and polytetrafluoroethylene, one finds instead disordered regions distrib-

uted in imperfect crystals, and formula (4.102) no longer holds true. Besides, formula (4.102) does not agree even qualitatively with experimental data at low temperatures. The use of formula (4.101) is more justifiable.

Attempts have been repeatedly made to find a correlation between the mean free path of phonons l and the sizes of spherulites. In actual fact, no such correlation exists. An important role in the determination of the character of the temperature dependence of the thermal conductivity of crystalline polymers is played by the crystallite sizes which restrict the mean free path of phonons at low temperatures. A number of crystalline polymers (for example, polyethylene) display a region in which $\kappa \propto T^3$. This confirms the supposition that in crystalline polymers at low temperatures there occurs a scattering of phonons at the boundaries of the crystallites. Yet, it is not clear at present why the thermal conductivity of some crystalline polymers increases with temperature and that of others (polyethylene, polyformaldehyde) decreases.

The available experimental data on thermal conductivity are not sufficient to give a reasonable explanation for the fundamentally different dependences of the thermal conductivity of various crystalline polymers on temperature. The mechanism of heat conduction in crystalline polymers will be more clearly understood if one can obtain continuous dependences $\kappa = f(T)$ for a number of crystalline polymers at temperatures ranging from the liquid-helium temperature to the melting temperatures of these polymers.

A distinctive feature of the temperature dependence of the thermal conductivity of amorphous polymers is the absence of the low-temperature peak typical of crystalline polymers and also the existence of a plateau at temperatures 4-15 K. Below 2 K the temperature dependence of κ is usually close to linear, which agrees well with the predictions of the theory of structural scattering. Above the plateau region the thermal conductivity again begins to increase with rise of temperature. The thermal conductivity of polymethyl methacrylate, a typical amorphous polymer, in the temperature range from 90 to 400 K has been studied by Eierman (32). The temperature dependence of the thermal conductivity of this polymer is shown in Figs. 4.8 and 4.9. To analyse the experimental data, expression (4.100) can be used, which is a modification of the results of the Klemens theory. A theoretical curve that describes the thermal conductivity of polymethyl methacrylate well has been plotted by using the following values of the parameters in formulas (4.96) through (4.100): $A/a = 22.4 \times 10^8 \text{ cm}^{-1}$; $T_0 = 7 \text{ K}$; the mean free path of transverse phonons $l_T = 7.1 \text{ \AA}$; $v_1 l_1 = 2.18 \times 10^{-2} \text{ cm}^2/\text{s}$. It has been demonstrated (31) that the mean free path due to one-dimensional longitudinal vibrations is equal to $l_1 = 7.3 \text{ \AA}$. The characteristic temperatures $\theta_3 = 39 \text{ K}$ and $\theta_1 = 171 \text{ K}$. If it is assumed that the

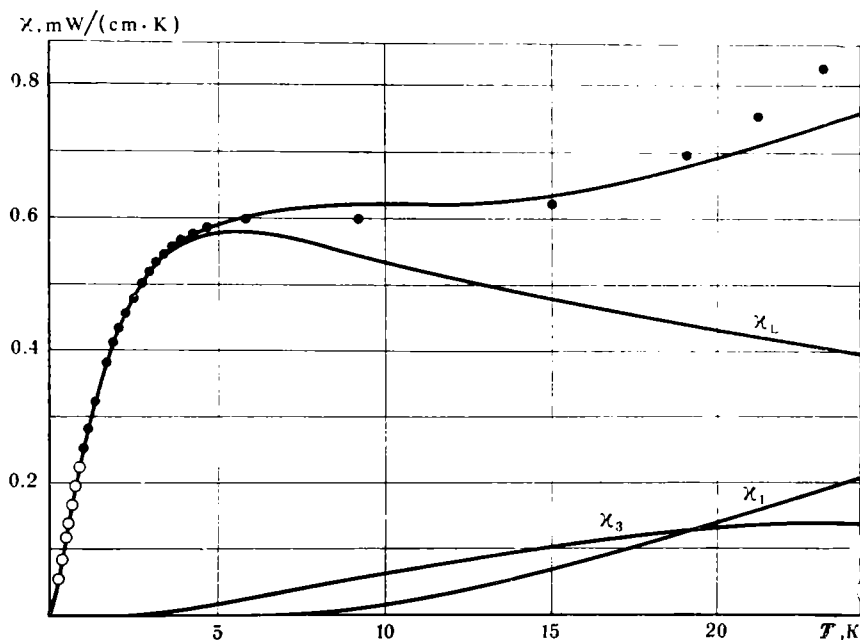


Fig. 4.8. Temperature dependence of the thermal conductivity coefficient of polymethyl methacrylate at low temperatures (κ_L is the part of thermal conductivity attributable to three-dimensional longitudinal vibrations; κ_3 is the contribution of three-dimensional transverse vibrations; κ_1 is the contribution of one-dimensional vibrations).

distance between polymeric chains (estimated from the density) is $a = 7.5 \text{ \AA}$, then it turns out that $A = 168$ and $A_T = 0.63$. Since these parameters are incorporated into the different terms (κ_L and κ_T) on the right-hand side of Eq. (4.100), it is obvious that the contribution of different types of phonons to the thermal conductivity is not the same. It is evident that the contribution of the transverse vibrations of the three-dimensional lattice to the total thermal conductivity of polymethyl methacrylate, κ , is very small (Figs. 4.8 and 4.9). The fact that $A \gg A_T$ implies that the three-dimensional transverse vibrations are strongly damped and the major contribution to the low-temperature thermal conductivity of polymethyl methacrylate comes from longitudinal waves. The fact that $A_T < 1$ creates certain difficulties in the application of the Klemens theory for the explanation of the temperature dependence of the thermal conductivity of polymethyl methacrylate since the mean free path of transverse phonons is $l_T = A_T a$. According to the Klemens theory, l must be of the same order of magnitude as the distance a between the vibrating units. Nevertheless, it is believed (31) that the values of $A_T < 1$ can be accounted for on the basis of the Ziman theory (33); Ziman related the mean free path of phonons to the change of

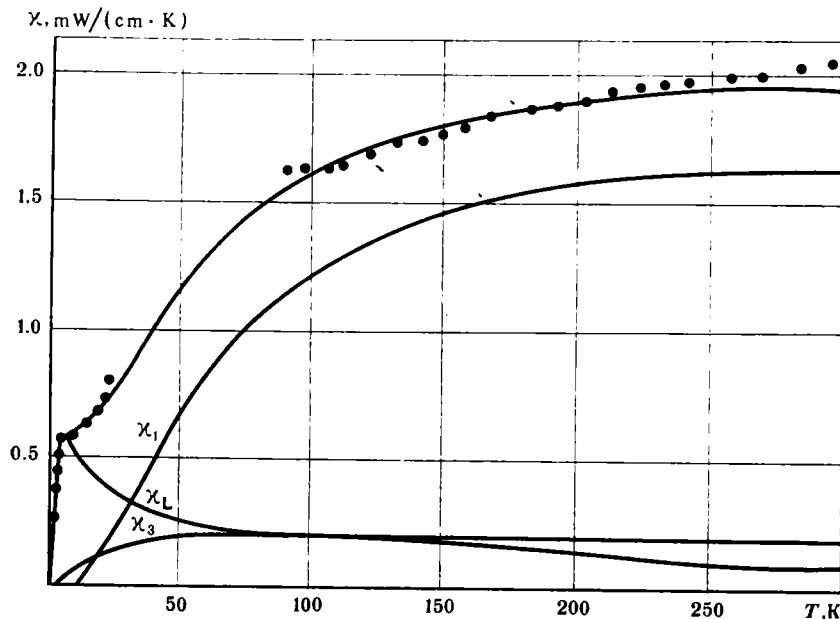


Fig. 4.9. Temperature dependence of the thermal conductivity coefficient of polymethyl methacrylate over a wide temperature range. The symbols are the same as in Fig. 4.8.

sound velocity in the amorphous region. For the values of $A_T < 1$ to be explained, one has to assume that large variations in the velocity of transverse waves are possible and that the correlation length for such variations is very small—of the same order of magnitude as a . From Figs. 4.8 and 4.9 it can be seen that the largest contribution to the low-temperature thermal conductivity of polymethyl methacrylate comes from the term due to longitudinal phonons. However, at higher temperatures (above 90 K) the contribution of κ_L to the total thermal conductivity becomes small, and the term due to one-dimensional vibrations begins to play a dominant role. This helps one understand why the orientation of amorphous polymers leads to a considerable increase in their thermal conductivity at high temperatures and does not substantially affect κ near the liquid-helium temperature.

Since the mean free path associated with three-dimensional vibrations and calculated for the region of high temperatures is found to be of the same order of magnitude as a , it follows that this result agrees well with the idea of elementary thermal resistances used by Eierman (26, 27) in his analysis of the thermal conductivity of polymers. Analysis of the theoretical conceptions underlying formula (4.100) leads one to the conclusion that the quantity $1/\kappa_1$ plays a role analogous to that of thermal resistance due to covalent bonds in the

Eierman model. The quantities $1/\kappa_L$ and $1/\kappa_3$ are to a certain extent analogous to the thermal resistances of secondary bonds. It is interesting to note that the ratio of the thermal conductivity due to one-dimensional vibrations to the thermal conductivity associated with three-dimensional vibrations is 10:1 at 300 K, which fits well the results following from the Eierman theory.

There is a considerable discrepancy between the theoretical values of κ and the experimental data at temperatures $T < 1$ K, at which the observed dependence of κ on temperature is stronger than the dependence of the type $\kappa \approx T$ predicted by theory. Indeed, Stephens and his coworkers (34) found that below 1 K for polymethyl methacrylate, as for some other amorphous materials (polystyrene, SiO_2 , selenium), the thermal conductivity depends on temperatures as follows:

$$\kappa \propto T^n \quad (4.103)$$

where $n = 1.8$.

For all amorphous materials for which the dependence (4.103) is valid one can observe a super-Debye excess heat capacity for the same temperature range (below 1 K). The possibility cannot be excluded that a dependence of the type (4.103) and the presence of the super-Debye heat capacity at $T < 1$ K are features common to amorphous materials and do not depend on the chemical structure.

In spite of some uncertainty in the interpretation of the non-linear temperature dependence of κ below 1 K, the mechanism of heat conduction in amorphous polymers has been clarified in greater detail than in the case of crystalline polymers.

4.3. Thermal Expansion of Polymers

4.3.1. Thermal Expansion of Solids

Thermal expansion is the change in the dimensions and shape of solids caused by a change of temperature. Any increase in temperature leads to an increase in the amplitude of vibrations of atoms about their equilibrium positions. When considering thermal expansion the assumption that the vibrations of atoms are sinusoidal (harmonic) in character proves to be insufficient. The factor responsible for the thermal expansion of solids is the anharmonic nature of atomic vibrations. The potential energy of two neighbouring vibrating atoms when they are displaced a distance x from the equilibrium position at a temperature of 0 K may be represented in the following form (1):

$$U(x) = \bar{f}x^2 - gx^3 - hx^4 \quad (4.104)$$

where \bar{f} is the quasi-elastic force coefficient ($f = -\bar{f}x$ in the case of harmonic oscillations); g is the anharmonicity factor.

The second term on the right-hand side of expression (4.104) takes account of the asymmetry of mutual repulsion, while the third term allows for the "attenuation" of vibrations at high amplitudes. If the displacements of atoms from their equilibrium positions, x , are small, then the terms involving x^3 and x^4 may be neglected as compared with the term with x^2 and the vibrations will be harmonic. With relatively large displacements from equilibrium positions the vibrations become anharmonic, and these terms in the expansion can no longer be neglected. Let us find the average displacement $\langle x \rangle$ of atoms from their equilibrium positions, this being what determines the change in the size of solids with a change in temperature (here use is made of the Boltzmann distribution function, which allows one to average out the values of any physical quantity with account being taken of the thermodynamic probability of the corresponding values):

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x e^{-U(x)/kT} dx}{\int_{-\infty}^{\infty} e^{-U(x)/kT} dx} \quad (4.105)$$

If the displacements of atoms are small enough (the anharmonicity of their vibrations is low), the integrand functions in expression (4.105) can be expanded into a series, and for the average displacement $\langle x \rangle$ the following expression is obtained (1):

$$\langle x \rangle = \frac{3kTg}{4\bar{f}^2} = \varepsilon_T \quad (4.106)$$

where ε_T is the thermal expansion.

The coefficient of volume thermal expansion, or volume expansivity, is given by

$$\beta = 3\alpha = \frac{3gk}{4\bar{f}^2} \quad (4.107)$$

where α is the coefficient of linear thermal expansion or linear expansivity.

From expression (4.107) it is seen that the thermal expansion of solids is a phenomenon caused by the anharmonicity of atomic vibrations. If no anharmonicity is present (the anharmonicity factor $g = 0$) and the atoms vibrate harmonically, then the thermal expansion coefficient becomes zero.

In the equilibrium state the lattice vibrations occur in such a manner that the solid occupies a volume to which the minimum of Helmholtz free energy corresponds. With a rise in temperature the amplitudes of vibrations of atoms in the lattice and, hence, their average displacement $\langle x \rangle$ from their equilibrium positions increase.

The anharmonic terms in expression (4.104) make such a contribution to the value of the free energy that it may be far from minimal. As a result, the solid will change its dimensions until its volume is such that it corresponds to the minimum of the potential energy.

The theory of the thermal expansion of solids is discussed in greater detail by Leibfried (22).

4.3.2. Equations of State for Solids

The thermal expansion coefficient is intimately connected with the main parameters of the equations of state of solids. To calculate the thermal volume expansion coefficient β of an isotropic solid we shall make use of the thermodynamic relations:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = 3\alpha \quad (4.108)$$

Let us consider the product of the thermal volume expansion coefficient and the isothermal compressibility K_T :

$$\beta K_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \left[-V \left(\frac{\partial P}{\partial V} \right)_T \right] \quad (4.109)$$

where P is the pressure.

It is known that

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (4.110)$$

The Helmholtz free energy is defined as

$$F = U - TS \quad (4.111)$$

From relations (4.109) through (4.111) we find that

$$\beta K_T = \frac{\partial^2 F}{\partial V \partial T} \quad (4.112)$$

The expression for the Helmholtz free energy can be represented as the sum of two terms, one of which depends on temperature and the other not. Assuming that the temperature-dependent part of the Helmholtz free energy of a solid is due to lattice vibrations, we can write:

$$F = U_0 + \sum_j \ln \left\{ 1 - \exp \left(- \frac{h\nu_j}{kT} \right) \right\} \quad (4.113)$$

where U_0 is the sum of the zero-point energy and the non-thermal part of the internal energy.

The zero-point energy is defined as the energy of the lattice at $T = 0$ K. This energy corresponds to the lowest quantum-mechanical state and has a quantum nature. Even at absolute zero the lattice

of a solid has a zero-point energy composed of kinetic and potential energies. The classical concept of a crystal lattice with atoms located at its points, whose vibrations are stopped at absolute zero, is incorrect. From quantum-mechanical considerations it follows that the vibrational motion of atoms is retained at absolute zero. The energy of the lowest quantum-mechanical state (the zero-point energy) is determined by the condition which states that the sum of the kinetic and potential energies must have a minimum. At low temperatures, when the kinetic energy of atoms is low, the positions of atoms in space appear to be "smeared out", which leads to an increase in the potential energy. The zero-point energy is, to a certain extent, a measure of such smearing-out. The smearing-out of the positions of atoms in space will be especially great if the mass of the atoms is small. It should be pointed out that the zero-point energy can reach relatively high values. It can be compared with the thermal energy of atoms at room temperature.

Using relations (4.109) through (4.113), we get:

$$V\beta K_T = \sum_j \gamma_j \frac{dE_j}{dT} \quad (4.114)$$

where the summation is carried out over all the normal lattice vibrations; E_j is the energy of the j th linear oscillator; the parameter γ_j is called the Grüneisen constant. The Grüneisen constant (or the Grüneisen gamma) shows the relationship between the frequencies of normal vibrations and the volume of the solid:

$$\gamma_j = -\frac{V}{v_j} \left(\frac{\partial v_j}{\partial V} \right)_T = -\frac{d \ln v_j}{d \ln V} \quad (4.115)$$

It is sometimes presumed that all γ_j are equal. This supposition is tantamount to assuming that the change in volume leads to a relative change in frequency which is the same for all vibrations. In such a case, expression (4.114) takes the form:

$$V\beta K_T = \gamma \sum_j \frac{dE_j}{dT} \quad (4.116)$$

Hence,

$$V\beta K_T = \gamma C_v \quad (4.117)$$

The last expression is often written down in the form

$$\beta = \gamma \frac{C_v}{VK_T} \quad (4.118)$$

and is called the Grüneisen relation. From this equation it follows that the volume expansion coefficient is directly proportional to the heat capacity. Since at $T = 0$ K the heat capacity $C_v = 0$, it evi-

dently follows that in this case the volume expansion coefficient must vanish, which is in keeping with the third law of thermodynamics.

In the Grüneisen approximation γ is assumed to be a weakly varying function of volume. It is sometimes believed that the Grüneisen constant is practically independent of temperature. But the Grüneisen assumption that all γ_j are equal is not sufficiently accurate. Therefore, the concept of the mean value γ_m of the Grüneisen constant has been introduced. It has been demonstrated (35) that γ_m depends on temperature. In his calculations (35), Barron proceeded from the Born-von Kármán theory. A crystal consisting of N atoms is regarded by him as an ensemble composed of $3N$ harmonic oscillators with frequencies of normal vibrations equal to ν_j . The equation of state is written in this case in the following way:

$$PV = -V E'_0(V) + \sum_{j=1}^{3N} \gamma_j \frac{h\nu_j}{\exp\left(\frac{h\nu_j}{kT}\right) - 1} \quad (4.119)$$

where P is the pressure; V is the volume; $E_0(V)$ is the non-thermal contribution to the internal energy of the crystal.

Without resorting to the Grüneisen assumption of the equality of all parameters γ_j , we can calculate the mean value of the Grüneisen constant:

$$\gamma_m = \sum_{j=1}^{3N} \gamma_j \frac{h\nu_j/kT}{\exp(h\nu_j/kT) - 1} \bigg/ \sum_{j=1}^{3N} \frac{h\nu_j/kT}{\exp(h\nu_j/kT) - 1} \quad (4.120)$$

Employing this relation and the conceptual model of the interaction potential, Barron has shown that $\gamma = f(T)$.

In the temperature region $T \ll 0.2\theta$ when $kT \ll h\nu_j$, only long acoustic waves are excited in the lattice and the solid may be considered as a continuum. In this case the Grüneisen constant can be represented as a function of the Debye characteristic temperature:

$$\gamma = -\frac{d \ln \theta}{d \ln V} = -\frac{V}{\theta} \cdot \frac{d\theta}{dV} \quad (4.121)$$

From the last equality it follows that the Grüneisen constant takes account of the effect of the volume change on the Debye temperature. In fact, this concept is a very rough model of thermal expansion (36). Different lattice vibrations are influenced in different ways by thermal expansion. The Grüneisen constant for longitudinal elastic lattice waves is, as a rule, much larger than for transverse waves. Therefore, the contributions from different modes of lattice vibrations to thermal expansion is found to be different.

4.3.3. Thermal Expansion of Amorphous Polymers

There is as yet no sufficiently rigorous and consistent theory of the thermal expansion of polymers. The major proportion of theoretical and experimental works are devoted to the study of glass transition and the variation of the thermal expansion coefficient of polymers near T_g . It is sometimes presumed that polymers have two thermal expansion coefficients. One of them is taken, β_g , to be independent of temperature at $T < T_g$, and the second, β_l , to be weakly dependent on temperature at $T > T_g$ and greater than the first. If we denote the volume expansion coefficients above and below the glass-transition temperature by β_l and β_g , then, according to Simha and Boyer (37),

$$(\beta_l - \beta_g) T_g = \Delta\beta T_g = K \quad (4.122)$$

where K may be regarded as a fraction of the free volume.

It has been found that for polymers, in which the molecular motion below T_g is not sharply pronounced, the parameter K assumes values varying about 0.113. However, relation (4.122) is not fulfilled at all times. For example, it does not hold for the series of polyalkyl methacrylates, for which K falls off with increasing length of the side chain. It is believed that the factor responsible for this deviation from the Simha-Boyer rule is the intensive motion of the side chains below T_g . Simha and Boyer believe that, as a result of the motion of the side chains, polyalkyl methacrylates in the glassy state retain an excess free volume, which leads to values of β_g much higher than usual. This must bring about a decrease in K . Therefore, it is suggested (38) that formula (4.122) be written in the form $(\beta_l - \beta_{g1}) \times T_g = K$, where β_{g1} is the expansion coefficient at temperatures below the temperature at which the side groups regain their mobility. Dilatometric measurements (38) show that, apart from the glass-transition temperature ($T_g = 376$ K), polymethyl methacrylate also displays temperature transitions at 288 K and 143 K. If, instead of β_{g1} , we use the value of $3\alpha_{g1}$ measured at $T < 143$ K, then $3(\alpha_l - \alpha_{g1}) T_g = 0.12$, which is in satisfactory agreement with the Simha-Boyer rule (42).

The Simha-Boyer formula is based on the assumption that the thermal expansion of polymers near T_g can be described with the aid of only two coefficients, β_l and β_g which must be practically independent of temperature. At the same time, experimental data show that the thermal expansion coefficients of polymers vary with temperature below and above the glass-transition temperature. These data indicate that even near the liquid-helium temperature the thermal expansion coefficients of all the polymers studied vary with temperature and tend to zero at $T \rightarrow 0$.

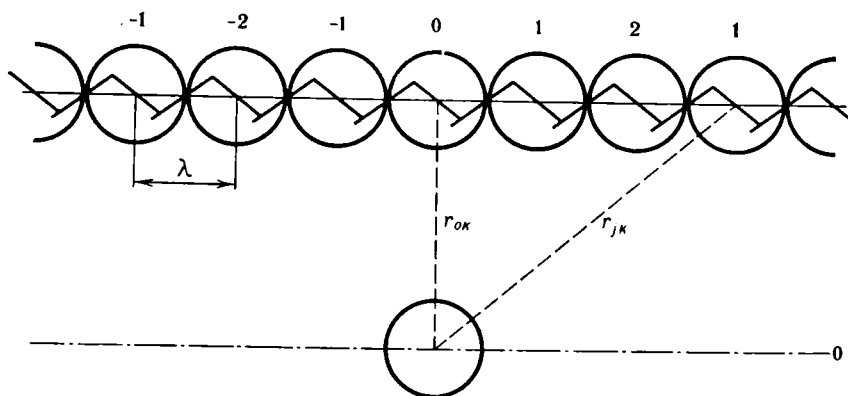


Fig. 4.10. The interacting-chain model (λ is the distance between the neighbouring centres along the chain; r_{0k} is the distance between the nearest centres of force of neighbouring chains; r_{jk} is the distance between the centre of forces at the coordinate origin and the j th centre in the k th shell).

The problem of the thermal expansion of amorphous polymers has been examined by Ishinabe and Ishikawa (39) on the basis of conceptual models. They assumed that polymeric chains in the amorphous state form a hexagonal (coordination number 6) or tetragonal (coordination number 4) lattice. These authors assumed the existence of an asymmetry of the field of dispersion forces associated with the coupled interaction between the repeating units of the various chains. The total potential energy was determined through the summation of coupled interactions throughout the entire lattice, with the exception of the energy of each polymeric chain. This treatment is, in effect, analogous to that based on the use of the Einstein model for solids and allows one to describe the thermodynamic properties of polymers in the glassy state with account taken of the part played by the van der Waals volume.

Let us consider in more detail the basic premises of the theory proposed by Ishinabe and Ishikawa, since they are typical of other theoretical investigations. Since in amorphous polymers there exists a short-range order (and, possibly, ordered regions as well), it is assumed that at a certain distance the repeating units of polymeric chains arrange themselves parallel to one another, form *trans*-conformations and build a hexagonal lattice (Fig. 4.10). Furthermore, it is presumed that a polymer is a single-phase system consisting of N homogeneous n -dimensional chains, each of which may be regarded as a set of n centres of mass. Each of these centres can move only in a plane perpendicular to the chain axes. The cross-sectional area of such a hexagonal lattice formed by polymeric chains is depicted in Fig. 4.11, with the size of the cells and the position of

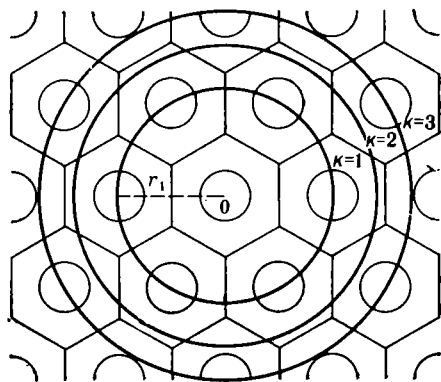


Fig. 4.11. The cross section of the hexagonal lattice formed by polymeric chains.

the shells rather strictly defined. The volume of one cell is

$$v = \lambda \gamma_c r_{0k}^2$$

where λ is the distance between two neighbouring centres of force along the chain; γ_c is a geometric factor equaling 0.866 for the hexagonal lattice and 1 for the tetragonal lattice; r_{0k} is the distance between the nearest centres of force of the neighbouring chains. In both types of lattice the shells are situated at a distance $\sqrt{k} \cdot r$, where $k = 1, 2, 3, \dots$

The potential energy of interaction of two centres, one of which is located at the coordinate origin and the other (the j th centre) in the k th shell, can be represented by a potential of the Lennard-Jones type:

$$\varphi_{jk} = \varepsilon^* f_{jk} \left[\left(\frac{r^*}{r_{jk}} \right)^{12} - 2 \left(\frac{r^*}{r_{jk}} \right)^6 \right] \quad (4.123)$$

where ε^* and r^* are parameters characterizing the energy and distance; f_{jk} is a factor taking account of the asymmetry of the field of dispersion forces in pair interactions.

The approximation for f_{jk} deduced from the London equation for the angular dependence of dispersion forces has the following form:

$$f_{jk} = 1 - 2kP_{jk} + k^2(5P_{jk} - 1) \quad (4.124)$$

where

$$P_{jk} = \frac{3}{2} \cdot \frac{r_h^2}{r_{jk}^2} - 1 \quad (4.125)$$

$$k = \frac{\alpha_{||} - \alpha_{\perp}}{3\alpha} \quad (4.126)$$

Here $\alpha_{||}$ and α_{\perp} are the polarizabilities of point centres in directions parallel and perpendicular to the chain axis, respectively; α is the average value of polarizability; $r_h = r_{0k}$ is the shortest distance between a given point centre and the k th chain.

Assuming the additivity of pair interactions and disregarding intrachain interactions, we can define the lattice energy as

$$\Phi = \frac{Nn\varepsilon^*}{2} \sum_{k=1}^{\infty} \sum_{j=-\infty}^{\infty} n_k f_{jk} \left[\left(\frac{r^*}{r_{jk}} \right)^{12} - 2 \left(\frac{r^*}{r_{jk}} \right)^6 \right] \quad (4.127)$$

where

$$r_{jk}^2 = r_k^2 + (j\lambda)^2$$

Since the summation in Eq. (4.127) is carried out for the case $r_k > 2\lambda$, this equation may be written down as follows:

$$\Phi = \frac{Nnz\varepsilon^*r^*}{2\lambda} \left[A\xi \left(\frac{V^*}{V} \right)^{11/12} - B\eta \left(\frac{V^*}{V} \right)^{5/2} \right] \quad (4.128)$$

where the characteristic volume V^* is determined by the expression $V^* = \lambda\gamma_c (r^*)^2$; the constants A and B and the coordination number z have the following values: $A = 0.775$, $B = 2.654$, $z = 6$ for the hexagonal lattice and $A = 0.791$, $B = 3.063$, $z = 4$ for the tetragonal lattice. The parameters ξ and η are found from the relations:

$$\xi = 1 - 0.751k + 0.878k^2 \quad (4.129)$$

$$\eta = 1 - 0.502k + 0.255k^2 \quad (4.130)$$

Assuming that the polymeric chain consists of q units, each of which moves independently, we find that the average potential energy of such a kinetic unit is equal to $U(0) = 2\Phi/Nq$. In calculating the potential energy account is taken only of the interactions between the closest chains. From the original premises given above the following equation of state is deduced (39):

$$\begin{aligned} \frac{PV}{T} = s \left[1 - 0.831 \left(\frac{\xi}{\eta} \right)^{1/6} \left(\frac{V^*}{V} \right)^{1/2} \right]^{-1} + \\ + \frac{z\varepsilon^*r^*}{2\lambda kT} \left[A'\xi \left(\frac{V^*}{V} \right)^{1/2} - B'\eta \left(\frac{V^*}{V} \right)^{5/2} \right] \end{aligned} \quad (4.131)$$

where $A' = 4.263$, $B' = 6.635$ for the hexagonal lattice and $A' = 4.351$ and $B' = 7.658$ for the tetragonal lattice; the parameter s characterizes the chain flexibility ($s = q/n$).

If the point centre has σ bonds, the parameter s_0 is introduced: $s_0 = s/\sigma = q/n\sigma$. This parameter can have values ranging from 0 to 1. For rigid molecules $s_0 = 0$ and for highly flexible molecules $s_0 = 1$. If we introduce the reduced temperature \tilde{T} , the reduced volume \tilde{V} and the reduced pressure \tilde{P} , which are given by

$$\tilde{T} = \frac{2s\lambda kT}{z\varepsilon^*r^*}; \quad \tilde{V} = \frac{V}{V^*}; \quad \tilde{P} = \frac{2\lambda V^*P}{z\varepsilon^*r^*} \quad (4.132)$$

then the reduced equation of state can be written as follows:

$$\begin{aligned} \frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left[1 - 0.831 \left(\frac{\xi}{\eta} \right)^{1/6} (\tilde{V})^{-1/2} \right]^{-1} + \\ + [A'\xi\tilde{V}^{-11/12} - B'\eta\tilde{V}^{-5/2}] \tilde{T}^{-1} \end{aligned} \quad (4.133)$$

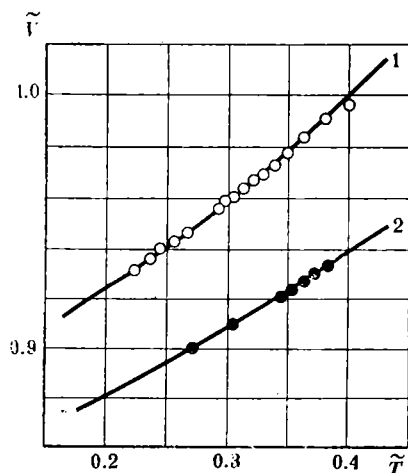


Fig. 4.12. Dependence of the reduced volume \tilde{V} on the reduced temperature T for the hexagonal (1) and tetragonal (2) lattices (\circ —polystyrene; \bullet —polymethyl methacrylate).

where the parameters η and ξ are close to unity (for example, $\xi = 1.035$ and $\eta = 1.023$ for polystyrene, and $\xi = 0.978$ and $\eta = 0.985$ for polyvinyl chloride).

At atmospheric pressure the left-hand side of Eq. (4.133) is very small and may be neglected as compared to the terms on the right-hand side of the equation. Then, assuming ξ and η to be equal to unity, we get an approximate expression:

$$\tilde{T} = -[1 - 0.831\tilde{V}^{-1/2}][A'\tilde{V}^{-11/12} - B'\tilde{V}^{-5/2}] \quad (4.134)$$

Equation (4.134) gives the relation between the van der Waals volume and the temperature at atmospheric pressure. The cubic expansion coefficient β can be found by differentiating this equation with respect to temperature:

$$\frac{1}{\tilde{\beta}} = [5.5A'\tilde{V}^{-11/12} - 2.5B'\tilde{V}^{-5/2}] - 2.493[2A'\tilde{V}^{-6} - B'\tilde{V}^{-3}] \quad (4.135)$$

The reduced cubic expansion coefficient $\tilde{\beta}$ is given by

$$\tilde{\beta} = \frac{1}{\tilde{V}} \left(\frac{\partial \tilde{V}}{\partial \tilde{T}} \right) = \frac{z(1-f_0)\epsilon^*r^*}{2s\lambda k} \beta \quad (4.136)$$

where f_0 is the relative free volume.

Thus, the thermodynamic properties of amorphous polymers in the glassy state can be described by Eqs. (4.134) and (4.135) if the values of the molecular parameters r^* , ϵ^* , and z are known. The values of r^* and ϵ^* can be calculated theoretically (39) through the use of certain experimental data. The results of such calculations for some amorphous polymers are given below.

	r^* , Å	s_0	ε^*/k , K	Type of lattice
Polystyrene	9.03	0.81	184.2	Hexagonal
Polymethyl methacrylate	7.89	0.66	229.2	Tetragonal
Polyvinyl chloride	6.11	0.34	134.9	Hexagonal

The results of theoretical calculations agree well with experimental data (40) for amorphous polymers, such as polymethyl methacrylate and polystyrene (see Fig. 4.12).

4.3.4. Thermal Expansion of Crystalline Polymers

It is obvious that the thermal expansion coefficient of a crystalline polymer must be dependent not only on volume or temperature but also on the degree of crystallinity. If the polymer is neither completely crystalline nor completely amorphous, its specific volume V can be represented as a linear combination of the specific volumes of crystalline, V_1 , and amorphous, V_2 , regions. If these regions are in equilibrium at the same temperature and pressure, we can write (see Chapter 2):

$$V = \lambda V_1 + (1 - \lambda) V_2$$

where λ is the so-called degree of crystallinity by weight (or mass) ($\lambda = m_1/m$, where m_1 is the total mass of crystalline regions in the sample of a given polymer, and m is the mass of the entire sample).

Let us divide both sides of the above equation by V_1^0 (the specific volume of a fully crystalline polymer at $T = 0$ K and $P = 0$) (41). Introducing the dimensionless parameters

$$X = \frac{V}{V_1^0}; \quad X_1 = \frac{V_1}{V_1^0}; \quad X_2 = \frac{V_2}{V_1^0}$$

we transform the equation for the specific volume:

$$X = \lambda X_1 + (1 - \lambda) X_2 \quad (4.137)$$

The thermal expansion coefficient will in this case assume the form:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{X} \left(\frac{\partial X}{\partial T} \right)_p \quad (4.138)$$

Equation (4.138) will then be written in the following manner:

$$\beta = [\lambda X_1 \beta_1 + (1 - \lambda) X_2 \beta_2] / X \quad (4.139)$$

The subscripts 1 and 2 refer, respectively, to the crystalline and amorphous regions of the polymer:

$$\beta_1 = \frac{1}{X_1} \left(\frac{\partial X_1}{\partial T} \right)_p; \quad \beta_2 = \frac{1}{X_2} \left(\frac{\partial X_2}{\partial T} \right)_p$$

Assuming that λ is a constant quantity, we can, via Eq. (4.139), calculate the thermal expansion coefficient β for a given degree of

crystallinity if the parameters β_1 , β_2 , X_1 , and X_2 are known. For polyethylene these parameters can be calculated theoretically by means of the available equations of state for completely crystalline and completely amorphous polymers. An equation of the following type holds for both phases of polyethylene (41):

$$P(X, T) = P_0(X) + g(X) T \quad (4.140)$$

where $P_0(X)$ is the pressure at 0 K, and the product $g(X) T$ represents the thermal contribution to the pressure (P_T) at given volume and temperature.

The form of the two functions in Eq. (4.140) depends on the ratio of the crystalline to amorphous regions. Since $(\partial P / \partial T)_X = \beta B_T$, where $B_T = -X (\partial P / \partial X)_T$, it follows that Eq. (4.140) yields the following expression for β :

$$\beta = P_T / (T B_T) \quad (4.141)$$

For crystalline polymers the principle of corresponding states holds in some cases, a circumstance that enables one to use Eq. (4.140) with the reduced variables.

There also exist other methods of describing the thermodynamic properties of crystalline polymers, in which such polymers are treated as three-dimensional crystals.

References

1. Kittel, C., *Introduction to Solid State Physics*, John Wiley, New York, 1976.
2. Debye, P., *Ann. der Physik*, **39**, 4, 789 (1912).
3. Born, M. and Th. Kármán, *Phys. Z.*, **13**, 5, 297 (1912).
4. Wunderlich, B. and H. Baur, *Heat Capacities of Linear High Polymers*, Springer-Verlag, Berlin, Heidelberg, New York, 1970.
5. Tarasov, V. V., *Zhur. Fiz. Khim.*, **24**, 1, 111 (1950).
6. Tarasov, V. V., *Zhur. Fiz. Khim.*, **27**, 9, 1430 (1953).
7. Tarasov, V. V., *New Problems of the Physics of Glass*, Gosstroizdat, Moscow, 1959 (in Russian).
8. Wunderlich, B., *J. Chem. Phys.*, **37**, 10, 2429 (1962).
9. Tucker, J. E. and W. Rees, *J. Chem. Phys.*, **46**, 4, 2388 (1967).
10. Lifshitz, I. M., *Zhur. Eksper. i Teoret. Fiz.*, **22**, 4, 475 (1952).
11. Landau, L. D. and E. M. Lifshitz, *Continuum Mechanics*, Gostekhizdat, Moscow and Leningrad, 1944 (in Russian).
12. Stockmayer, W. H. and C. E. Hecht, *J. Chem. Phys.*, **21**, 11, 1954 (1953).
13. Rees, W., *J. Macromol. Sci.*, **3**, 7, 1257 (1969).
14. Perepechko, I. I., *Low-Temperature Properties of Polymers*, Mir Publishers, Moscow and Pergamon Press, Oxford, 1980.
15. Rosenstock, H. B., *J. Phys. Chem. Solids*, **23**, 6, 659 (1962).
16. Choy, C. L., R. G. Hunt, and G. L. Salinger, *J. Chem. Phys.*, **52**, 7, 3629 (1970).
17. Zoller, P., D. L. Fehl, and J. R. Dillinger, *Phys. Letters*, **32**, A, 4, 228 (1970).
18. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers Moscow, 1975.

19. Godovsky, Yu. K., *Thermophysical Properties of Polymers*, Khimiya, Moscow, 1976 (in Russian).
20. Peierls, R., *Ann. der Phys.*, **3**, 8, 1055 (1929).
21. Klemens, P., in: *Low Temperature Physics*, Berlin, 1956.
22. Leibfried, G., "Gittertheorie der mechanischen und thermischen Eigenschaften der Kristalle" ("Macroscopic Theory of Mechanical and Thermal Properties of Crystals"), in: *Handbuch der Physik*, Bd. VII, Teil 1, Berlin, Springer-Verlag, 1955.
23. Mogilevsky, B. M. and A. F. Chudnovsky, *Thermal Conductivity of Semiconductors*, Nauka, Moscow, 1972 (in Russian).
24. Leibfried, G. and E. Schloemann, *Nachr. Akad. Wiss. Göttingen*, **2a**, 4, 71 (1954).
25. Eierman, K., K. H. Hellwege, and W. Inappe, *Koll.-Z.*, **174**, 2, 134 (1961).
26. Eierman, K., *Koll.-Z.*, **198**, 1-2, 5 (1964).
27. Eierman, K., *Koll.-Z.*, **199**, 2, 125 (1964).
28. Eierman, K., *J. Polymer Sci.*, C, **6**, 157 (1964).
29. Klemens, P. G., *Proc. Roy. Soc. (London)*, A, **208**, 1092, 108 (1951).
30. Klemens, P. G., in: *Physics of Non-Crystalline Solids*, ed. by J. A. Prins, Amsterdam, North-Holland Publ. Co., 1965.
31. Rees, W., *J. Appl. Phys.*, **37**, 8, 3227 (1966).
32. Eierman, K., *Kunststoffe*, **55**, 5, 335 (1965).
33. Ziman, J. M., *Electrons and Phonons*, Oxford University Press, Oxford, 1960.
34. Stephens, R. B., G. S. Gieloszyk, and G. L. Salinger, *Phys. Letters*, A, **38**, 3, 215 (1972).
35. Barron, T. H. K., *Phil. Mag.*, **46**, 378, 720 (1955).
36. Ziman, J. M., *Principles of the Theory of Solids*, Cambridge, 1964.
37. Simha, R. and K. F. Boyer, *J. Chem. Phys.*, **37**, 5, 1003 (1962).
38. Haldon, R. A. and R. Simha, *J. Appl. Phys.*, **39**, 3, 1890 (1968).
39. Ishinabe, T. and K. Ishikawa, *Japan J. Appl. Phys.*, **7**, 5, 462 (1968).
40. Hellwege, K. H., W. Knappe, and P. Lehman, *Koll.-Z.*, **183**, 2, 110 (1962).
41. Pastine, D. J., *J. Appl. Phys.*, **41**, 13, 5085 (1970).
42. Kan, K. N., *Problems of the Theory of Thermal Expansion of Polymers*, Izdat. LGU (Leningrad University Press), Leningrad, 1975 (in Russian).

Chapter 5

Electrical Properties of Polymers

5.1. Basic Concepts of the Dielectric Properties of Solids

The majority of polymers are typical dielectric materials. When they are placed in an electric field, an electric moment arises in them, i.e., electrical polarization takes place. The polarization of the unit volume of a dielectric, \bar{P} , can be represented by the following sum:

$$\bar{P} = \bar{P}_{\text{or}} + \bar{P}_{\text{def}} \quad (5.1)$$

where \bar{P}_{or} is the polarization due to the orientation of permanent dipoles (orientational polarization); \bar{P}_{def} is the deformational polarization, a polarization due to the distortion of electronic shells or to the displacement of atomic nuclei.

The permanent dipoles are characterized by the magnitude of the dipole moment p :

$$p = ql \quad (5.2)$$

where q is the magnitude of the charge; l is the separation of the charges.

In the absence of an electric field the permanent dipoles may be randomly distributed; the total dipole moment of such a system is zero. When an electric field is applied, there occurs a certain orientation of the dipoles and an orientation electric moment arises, characterized by the polarization vector \bar{P}_{or} . The role of permanent dipoles in polymers is played by polar groups. For instance, in the case of polyvinyl chloride the C—Cl group is such a dipole.

In non-polar dielectrics the electric moment P_{def} is generated when an electric field is applied. Under the influence of an electric field the electric charges in molecules (or in parts of molecules) of the dielectric are displaced and induced electric dipoles appear. The moment of an induced dipole, p , is directly proportional to the strength E_i of the applied electric field:

$$p = \alpha \bar{\epsilon}_0 E_i \quad (5.3)$$

where $\bar{\epsilon}_0$ is the permittivity of free space ($\bar{\epsilon}_0 = 8.85 \times 10^{-12}$ F/m); α is a certain coefficient called the polarizability of the molecule.

For any type of dielectric (except for ferroelectric materials) the polarization vector is connected with the field strength by a simple relation:

$$\bar{P} = \chi \varepsilon_0 \bar{E} \quad (5.4)$$

The dimensionless parameter χ is called the dielectric susceptibility. Sometimes, the product $\chi \varepsilon_0$ is called the dielectric susceptibility.

In a number of cases the dielectric susceptibility of non-polar dielectrics is equal to $\chi = n\alpha$, where n is the number of induced dipoles per unit volume and α is the polarizability of the molecule. The relation $\chi = n\alpha$ is approximate. A more accurate expression for χ will be derived at a later time.

The electrical properties of dielectrics are characterized by the electric moment arising when an electric field is applied. The deformational part P_{def} of this moment appears very rapidly, in 10^{-13} to 10^{-14} s. The time during which the orientational moment is set up depends to a considerable extent on the temperature, the shape of the molecules (or parts of molecules which have permanent dipole moments) and the forces of intermolecular interaction.

Of great importance in a consideration of the electrical properties of dielectrics is the calculation of the strength of the electric field acting on an atom or molecule. The strength of such a local field is given by

$$\bar{E}_i = \bar{E} + \frac{1}{3} \frac{\bar{P}}{\varepsilon_0} \quad (5.5)$$

where \bar{E} is the macroscopic field strength; the quantity \bar{P} characterizes the field arising from the polarization of all other atoms or molecules of the sample. It should be noted that formula (5.5) is strictly fulfilled only for crystals of the cubic system.

A considerable role in a description of the electrical properties of solid dielectrics is played not only by the macroscopic electric field strength \bar{E} inside the dielectric but also by the electric displacement \bar{D} . In anisotropic solids the electric displacement is a tensor. The relationship between the quantities \bar{D} and \bar{E} allows one to determine the dielectric constants of solids. For an isotropic material

$$\bar{D} = \varepsilon_0 \bar{E} + \bar{P} = \varepsilon_0 \bar{E} + \chi \varepsilon_0 \bar{E} = \varepsilon_0 \varepsilon \bar{E} \quad (5.6)$$

Hence the dielectric constant is equal to

$$\varepsilon = 1 + \chi \quad (5.7)$$

where $\chi = \bar{P}/(\varepsilon_0 \bar{E})$. In accordance with formula (5.5) we can write expression (5.3) for the induced dipole moment of a non-polar mole-

cule in the following form:

$$\bar{p} = \alpha \bar{\epsilon}_0 \left(\bar{E} + \frac{1}{3} \frac{\bar{P}}{\bar{\epsilon}_0} \right) \quad (5.8)$$

Then the electric moment of the unit volume of a dielectric may be defined as

$$\bar{P} = n\bar{p} = n\alpha \bar{\epsilon}_0 \bar{E} + \frac{1}{3} n\alpha \bar{P} \quad (5.9)$$

from which it follows that

$$\bar{P} = \frac{n\alpha}{1 - \frac{n\alpha}{3}} \bar{\epsilon}_0 \bar{E} \quad (5.10)$$

Comparing relations (5.4) and (5.10), we obtain:

$$\chi = \frac{n\alpha}{1 - \frac{n\alpha}{3}} \quad (5.11)$$

It is evident that at $n\alpha \ll 1$ the dielectric susceptibility $\chi \approx n\alpha$. The last relation is valid for rarefied gases. Formula (5.11) may be rewritten as

$$\frac{1}{3} n\alpha = \frac{\chi}{3 + \chi} \quad (5.11a)$$

Considering that $\chi = \epsilon - 1$, we obtain the well-known Clausius-Mosotti equation which agrees well with experiment in the case of crystals of the cubic system, and non-polar liquids and gases:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n\alpha}{3} \quad (5.12)$$

It has already been said that when a dielectric is introduced into an electric field the dipoles become oriented not instantaneously but during a certain interval of time. If the electric field is switched off, then, as a result of thermal motion, the polarization of the dielectric will decrease e times after some time τ . This phenomenon is known as the dielectric relaxation and τ is called the dielectric relaxation time. Obviously, the molecular polarizability α of the dielectric (and, hence, the parameters χ and ϵ) placed in a periodically varying electric field must depend on the period of variation of this field, $T = 2\pi/\omega$, the relaxation time τ and the relation between T (or ω) and τ .

The most efficient theory of dielectric relaxation has been worked out by Debye for polar liquids. He has shown that the polarizability due to the orientation of molecules may be represented in the form

$$\alpha = \frac{\alpha_0}{1 + i\omega\tau} \quad (5.13)$$

where α_0 is the static polarizability; τ is the relaxation time; ω is the frequency of the variation of the electric field.

From the Debye theory it follows that the polarization of polar molecules in a liquid does not occur instantaneously and is characterized by the relaxation time. For spherical molecules the dielectric relaxation time depends on the viscosity of the liquid η and its temperature T :

$$\tau = \frac{4\pi\eta a^3}{kT} \quad (5.14)$$

where a is the radius of the molecule. For the majority of polar liquids the relaxation time τ is of the order of 10^{-10} to 10^{-11} s.

Whereas the orientation of dipoles in liquids takes place comparatively freely and rapidly, in solids the orientation of molecules (or parts of molecules) with permanent dipole moments occurs much more slowly and is accompanied by relaxation processes having various relaxation times.

In the case of dielectrics which are subjected to the action of varying electric fields, the relationship between the electric displacement D and the electric field strength E can be represented in the following manner:

$$D = \bar{\epsilon}_0 \epsilon^* E \quad (5.15)$$

The complex dielectric constant or relative permittivity ϵ^* is given by

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (5.16)$$

The real part ϵ' of the complex dielectric constant (or relative permittivity) ϵ^* is sometimes called the dielectric constant; it characterizes the most important electrical properties of dielectrics. The imaginary part ϵ'' is called the dielectric loss factor; it characterizes the dissipation of the energy of electrical oscillations in a dielectric subjected to the action of a varying electric field. In this case, there arises a phase lag between the electric displacement vector D and the electric field strength E , described by the dielectric loss tangent or dissipation factor:

$$\tan \delta = \epsilon''/\epsilon' \quad (5.17)$$

The magnitude of the dielectric constant of polymers is determined by their chemical and physical structure and composition. The parameters that characterize the dielectric losses (ϵ'' and $\tan \delta$) depend on the specific features of molecular motion in polymers and, hence, on their chemical and physical structure.

5.2. Phenomenological Theory of the Dielectric Properties of Polymers

5.2.1. Fundamental Equations

Let us consider the relationship between the electric displacement D and the electric field strength in a polymeric dielectric. We shall make use of some concepts that have been developed for describing the processes of acoustic relaxation in polymers (1). Since the analogy between acoustic relaxation and dielectric relaxation is based on the detailed physical similarity of these processes, it is natural that the concepts expounded earlier (2) should be employed in a study of the dielectric properties of polymers.

The electric displacement in an isotropic medium may be represented as the following sum:

$$D = D_{\infty} + D_1 \quad (5.18)$$

where D_{∞} is the electric displacement in the dielectric material corresponding to a case where the frequency of electrical oscillations $\omega \rightarrow \infty$; D_1 is the "dissipation" part of the electric displacement.

The electric displacement D_{∞} is defined as follows:

$$D_{\infty} = \bar{\epsilon}_0 \epsilon'_{\infty} E \quad (5.19)$$

where ϵ'_{∞} is the dielectric constant measured at frequency $\omega \rightarrow \infty$.

The "dissipation" part of the electric displacement is given by

$$D_1 = \epsilon_0 \epsilon_1 E \quad (5.20)$$

where ϵ_1 is the dielectric constant of the dielectric. It must be a certain operator in a general form.

Representing the electric displacement as the sum of two terms is probably justified since the electric moment of the dielectric, resulting from the application of an electric field, has two components, one of which (the deformation component) is established very rapidly ($\approx 10^{-13}$ s).

It should be remarked that expressions for the electric displacement D such as (5.19) are, strictly speaking, valid only for steady (time-independent) electric fields. If the electric field E applied to a dielectric varies periodically with time, the electric displacement D at each point of the material at a given moment of time will depend not only on the electric field strength and the rate of its variation but also on the entire previous history of the material. If the period of variation of the electric field becomes commensurate with the time required for establishing a statistical equilibrium, then relaxation processes will play an active part in the material. It is obvious that the transition to equilibrium can occur in such a way that the relaxation processes are superimposed. Therefore, in a real polymeric

dielectric placed in a sinusoidally varying electric field the electric displacement vector must take account of the past history of the material in some way.

Thus, in order to describe the dielectric properties of polymeric dielectrics, use must be made of certain non-equilibrium values of D_1 different from the steady-state values of D_{01} , which correspond to steady (time-independent) electric fields.

Assuming that the departure of D_1 from the steady-state value D_{01} is not great, we can write the following relaxation equation:

$$\frac{\partial D_1}{\partial t} = -\frac{1}{\tau} (D_1 - D_{01}) \quad (5.21)$$

Equation (5.21) may be regarded as a corollary of the fundamental propositions of the thermodynamics of nonequilibrium (irreversible) processes. If the electric displacement D_1 is steady-state, then $\partial D_1 / \partial t = 0$ and $D_1 = D_{01}$. The parameter τ is the dielectric relaxation time.

In the case of periodic harmonic processes Eq. (5.21) becomes

$$i\omega\tau D_1 = -D_1 + D_{01} \quad (5.22)$$

From this equation it follows that

$$D_1 = \frac{D_{01}}{1 + i\omega\tau} \quad (5.23)$$

From a comparison of Eq. (5.23) with Eq. (5.20) it becomes evident that the dielectric constant ϵ_1 can be given in a complex form:

$$\epsilon_1 = \frac{\epsilon_{01}}{1 + i\omega\tau} \quad (5.24)$$

where ϵ_{01} is the "static" low-frequency value of the dielectric constant.

Real polymeric dielectrics are commonly described by a spectrum of relaxation times rather than by a single relaxation time. There are several reasons for the appearance of a relaxation time spectrum. They include unequal rates of relaxation processes in various portions of the material and the occurrence of different relaxation mechanisms. In the case of polymers, relaxation-time spectra probably appear as a result of the presence of long polymeric chains and the specificity of intermolecular interaction.

With an arbitrary number of relaxation processes, expression (5.24) may be written in the form:

$$\epsilon_1 = \sum_{j=1}^n \frac{\epsilon_{0j}}{1 + i\omega\tau_j} \quad (5.25)$$

Thus, taking cognizance of expressions (5.25), (5.18), (5.19), and (5.20), we get:

$$D = \bar{\epsilon}_0 \left\{ \epsilon_\infty + \sum_{j=1}^n \frac{\epsilon_{0j}}{1 + i\omega\tau_j} \right\} E \quad (5.26)$$

The expression enclosed in parentheses may be looked upon as an operator of the dielectric constant:

$$\hat{\epsilon} = \epsilon_\infty + \sum_{j=1}^n \frac{\epsilon_{0j}}{1 + i\omega\tau_j} \quad (5.27)$$

This operator can be presented in a differential form:

$$\hat{\epsilon} = \epsilon_\infty + \sum_{j=1}^n \frac{\epsilon_{0j}}{1 + \tau_j \frac{\partial}{\partial t}} \quad (5.28)$$

Comparing expressions (5.15), (5.16), (5.18), and (5.26) and separating the real and imaginary parts in expression (5.26), we arrive at the following formulas for ϵ' and ϵ'' :

$$\epsilon' = \epsilon_\infty + \sum_{j=1}^n \frac{\epsilon_{0j}}{1 + \omega^2\tau_j^2} \quad (5.29)$$

$$\epsilon'' = \sum_{j=1}^n \frac{\epsilon_{0j}\omega\tau_j}{1 + \omega^2\tau_j^2} \quad (5.30)$$

Formulas (5.29) and (5.30) indicate the presence of a discrete spectrum of dielectric relaxation times arising in a polymer placed in a varying electric field. In passing from the discrete to a continuous spectrum at $n \rightarrow \infty$, we obtain from expressions (5.29) and (5.30):

$$\epsilon' = \epsilon_\infty + \int_0^\infty \frac{H(\tau) d\tau}{1 + \omega^2\tau^2} \quad (5.31)$$

$$\epsilon'' = \int_0^\infty \frac{H(\tau) \omega\tau d\tau}{1 + \omega^2\tau^2} \quad (5.32)$$

where $H(\tau)$ is the density of the dielectric relaxation time spectrum.

Let us consider a case where $\omega\tau \rightarrow \infty$. Then $\epsilon' = \epsilon_\infty$ and $\epsilon'' \rightarrow 0$. For polymers this condition corresponds either to very high frequencies ($\omega \rightarrow \infty$, $\tau = \text{const}$) or to very low temperatures ($\omega = \text{const}$, $\tau \rightarrow \infty$). Thus, from phenomenological relaxation theory it follows that at low temperatures the dielectric constant ϵ' and

the corresponding losses determined by the parameter ε'' can be expected to decrease.

In the other limiting case where $\omega\tau \rightarrow 0$, which corresponds to low frequencies or relatively high temperatures, the quantity ε' increases, attaining the value

$$\varepsilon' = \varepsilon_{\infty} + \int_0^{\infty} H(\tau) d\tau \quad (5.33)$$

and ε'' tends to zero.

5.2.2. Dielectric Properties of a System with a Single Relaxation Time

The expressions for ε' and ε'' assume the simplest form in the case of a relaxation process characterized by a single relaxation time. If in Eqs. (5.29) and (5.30) one of the values of τ_j and one of the quantities ε_{0j} corresponding to this relaxation time are different from zero ($\tau_j \neq 0$; $\varepsilon_{0j} \neq 0$), then ε' and ε'' can be given by

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_1}{1 + \omega^2\tau^2} \quad (5.34)$$

$$\varepsilon'' = \frac{\varepsilon_1\omega\tau}{1 + \omega^2\tau^2} \quad (5.35)$$

It should be noted that formulas (5.34) and (5.35) coincide exactly with the corresponding Debye formulas (3, 4), though this is not obvious at first glance.

Let us consider the dependence of ε' on the parameter $\omega\tau = 2\pi(\tau/T)$, where τ is the relaxation time; T is the time of variation of the electric field in the dielectric. An analysis of equations that describe relaxation processes in polymers is preferably carried out in terms of $\omega\tau$. At $\omega\tau = 0$

$$\varepsilon' = \varepsilon_0 = \varepsilon_{\infty} + \varepsilon_1 \quad (5.36)$$

At $\omega\tau \rightarrow \infty$

$$\varepsilon' = \varepsilon_{\infty}$$

Thus, when the value of $\omega\tau$ changes from 0 to ∞ , the dielectric constant varies from ε_0 to ε_{∞} , i.e., decreases. Substituting ε_1 found from expression (5.36) into formulas (5.34) and (5.35), we obtain expressions for ε' and ε'' in a more usual, "canonical" form:

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2\tau^2} \quad (5.37)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_{\infty}) \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (5.38)$$

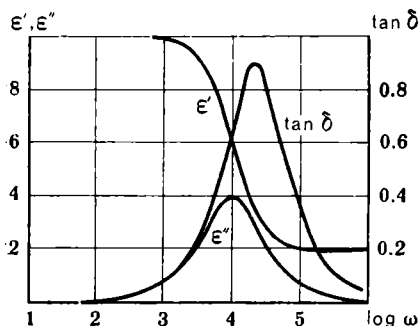


Fig. 5.1. Frequency dependences of ϵ' , ϵ'' and $\tan \delta$ calculated theoretically on the assumption that $\epsilon_0 = 10$, $\epsilon_\infty = 2$ and $\tau = 10^{-4}$ s.

Within the framework of the model under discussion the expression for the dielectric loss tangent has the form

$$\tan \delta = 2 \tan \delta_m \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \quad (5.39)$$

where

$$2 \tan \delta_m = \frac{\epsilon_0 - \epsilon_\infty}{\sqrt{\epsilon_0 \epsilon_\infty}} \quad (5.40)$$

The relaxation time τ_1 differs from the relaxation time τ in formulas (5.37) and (5.38):

$$\tau_1 = \tau \sqrt{\frac{\epsilon_\infty}{\epsilon_0}}$$

It is easy to see that $\tan \delta$ has a maximum ($\tan \delta_m$) at $\omega \tau_1 = 1$, while ϵ'' passes through a maximum at $\omega \tau = 1$. Typical frequency dependences of ϵ' , ϵ'' , and $\tan \delta$ calculated from formulas (5.37) through (5.39) on the assumption that $\epsilon_0 = 10$, $\epsilon_0/\epsilon_\infty = 5$ and $\tau = 10^{-4}$ s are presented in Fig. 5.1.

The Debye equations (5.37), (5.38), and (5.39) for ϵ' , ϵ'' , and $\tan \delta$ very closely resemble the corresponding expressions for the components of the complex elastic modulus (1, 4), the electric field strength E being analogous to the mechanical stress σ and the electric displacement D to the strain ϵ . In its turn, the complex dielectric constant is analogous to the complex compliance J^* .

As a rule, dielectric relaxations in polymers are associated with the presence of a relaxation-time spectrum. Apart from formulas (5.31) and (5.32), other methods of describing the dielectric properties of polymers are also used (4-10).

5.2.3. Temperature Dependence of Dielectric Properties

From the above expressions for ϵ' , ϵ'' , and $\tan \delta$ it can be seen that these parameters depend on the frequency and the relaxation time τ . The temperature dependence of dielectric properties is de-

terminated by the character of the dependence of relaxation time on temperature. If we assume that τ depends on temperature T in accordance with an expression of the type

$$\tau = \tau_0 e^{U/RT} \quad (5.41)$$

(where τ_0 is a constant quantity; U is the energy of activation; R is the universal gas constant), then Eqs. (5.37) and (5.38) may be written in the form:

$$\epsilon' = \epsilon_\infty^T + \frac{\epsilon_0^T - \epsilon_\infty^T}{1 + \omega^2 \tau_0^2 e^{2U/RT}} \quad (5.42)$$

$$(\epsilon'' = (\epsilon_0^T - \epsilon_\infty^T) \frac{\omega \tau_0 e^{U/RT}}{1 + \omega^2 \tau_0^2 e^{2U/RT}} \quad (5.43)$$

where ϵ_0^T and ϵ_∞^T are the corresponding dielectric constants at temperature T .

The plot of ϵ'' against $1/T$ is often used for the analysis. It has been shown (4) that if the difference $\epsilon_0 - \epsilon_\infty$ does not depend on temperature, then the area under the curve of the function $\epsilon'' = f(1/T)$ depends only on the activation energy and the parameter $\epsilon_0 - \epsilon_\infty$ and does not depend explicitly on frequency:

$$\int_0^\infty \epsilon'' d\left(\frac{1}{T}\right) = (\epsilon_0 - \epsilon_\infty) \frac{\pi R}{2U} \quad (5.44)$$

For polar molecules, from the Onsager, Fröhlich, and Debye theories it follows that

$$\epsilon_0 - \epsilon_\infty = A/T \quad (5.45)$$

where A is a constant.

In this case, the dependence of ϵ'' on $1/T$ appears to be more complicated (4). Apart from the area under the $\epsilon'' = f(1/T)$ curve, the magnitude of the activation energy of relaxation processes is also associated with the half-peak width of the curve. In fact, formula (5.38) can be rewritten in the form:

$$\epsilon'' = 2\epsilon_m'' \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (5.46)$$

If we introduce the notation $\epsilon_m''/\epsilon'' = r$, then $\omega\tau = r \pm \sqrt{r^2 - 1}$. It can be shown (1, 4) that

$$U = \frac{2.303R \log(r \pm \sqrt{r^2 - 1})}{\frac{1}{T_i} - \frac{1}{T_m}} \quad (5.47)$$

where T_i is the temperature corresponding to ϵ_i'' ; T_m is the temperature at which the maximum of ϵ'' occurs.

If we put $r = 2$, which corresponds to $\varepsilon'' = 0.5 \varepsilon_m''$, then

$$U = \frac{2.63}{\frac{1}{T_{0.5}} - \frac{1}{T_m}} \quad (5.48)$$

where $T_{0.5}$ is the temperature which corresponds to $\varepsilon'' = 0.5 \varepsilon_m''$ on the $\varepsilon'' = f(1/T)$ graph.

If the relaxation process cannot be described by a model that presupposes the existence of a single relaxation time, then the relationship between the activation energy and the half-peak width on the $\varepsilon'' = f(1/T)$ plot becomes more complicated.

5.3. The Mechanism of Dielectric Relaxation

One of the first scientists to study the mechanism of dielectric relaxation in solids was Debye, who assumed that molecular dipoles placed in a constant electric field may align themselves, at a first approximation, in two directions: parallel or antiparallel to the field. If no electric field is applied, both positions are equivalent and equal potential energies correspond to them. If the potential energy of the dipole is represented as a function of the angle of rotation, then it will be a curve with two equal minima separated by a maximum (the potential barrier), the height of which relative to the minimum will just determine the probability of the transition of the dipole from one position to the other (rotation through 180°). When an electric field is applied, the energies of the dipoles situated on each side of the potential barrier are changed. The dipoles parallel to the field have a lower potential energy (Fig. 5.2); and the dipoles antiparallel to the field will have a potential energy minimum lying somewhat higher. In such a case, the probabilities of a switchover from position 1 to position 2 and vice versa will not coincide. The dipoles will perform oscillations at frequency ν_0 about their equilibrium positions and their transition from one position to another will be associated with the possibility of rotation. A detailed examination of the process of jumping over the potential barrier leads one to the conclusion that the dielectric relaxation time depends on temperature in accordance with an equation of the type (5.41). This problem has been examined in detail by Fröhlich (4-10).

Models that describe the rotation of dipoles associated with the jump over the potential barrier hindering rotation are widely used to depict dielectric relaxations occurring in polymers. Conceptions of this kind are usually employed for the explanation of relaxation processes caused by the hindered rotation of side groups and also by the segmental mobility of the main chains.

The mechanism of dielectric relaxation processes in polymers has been studied in detail by Mikhailov and his coworkers (7). According

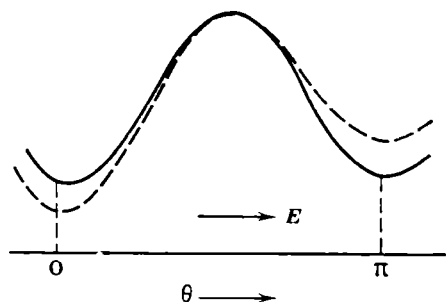


Fig. 5.2. The potential energy of a dipole as a function of the angle of rotation (the solid curve represents data in the absence of an electric field; the dashed curve represents data obtained with an applied electric field).

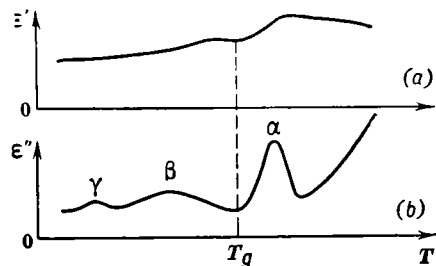


Fig. 5.3. Dependence of the low-frequency dielectric constant (a) and the dielectric loss factor (b) on temperature for a polar polymer.

to the terminology proposed by Mikhailov, two types of dielectric relaxation are possible in polymers: dipolar-segmental and dipolar-group. These processes give maxima on the temperature or frequency dependences of ϵ'' and $\tan \delta$. The relaxation processes in polymers are most often studied by carrying out measurements over a wide temperature range at several frequencies.

In amorphous polymers the most intense peak of ϵ'' or $\tan \delta$ occurs in the region of transition from the glassy to the rubbery (high-elastic) state. It is caused by the micro-Brownian motion of segments in polymeric chains. Dielectric losses of this kind are called dipolar-segmental losses. Dielectric relaxations caused by the localized movement of molecules are known as dipolar-group relaxations.

The terminology used in other countries for relaxation processes is different. Usually the dielectric loss peaks in the $\epsilon'' = f(T)$ or $\tan \delta = f(T)$ graphs, beginning with the most intense high-temperature peak (in the case of amorphous polymers), are designated by the Greek letters α , β , γ , δ , etc. (Fig. 5.3). Relaxation processes that manifest themselves when the temperature is lowered are accordingly labeled α , β , γ , δ , etc. In this convention, the dipolar-segmental process is called the α -relaxation. The dipolar-group process may correspond to the β -, γ - or δ -relaxation. The dielectric loss peaks situated in the region of secondary (β -) relaxation are usually due to the movement of side groups or small units of main chains. It has been suggested (11) that only the processes caused by the movement of side groups be referred to as β -relaxation.

One of the polymers in which there is observed the α -process at the high-temperature end and the β -process at the low-temperature end is polyvinyl chloride.

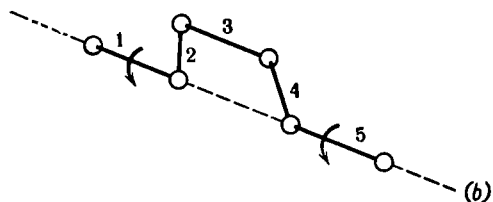
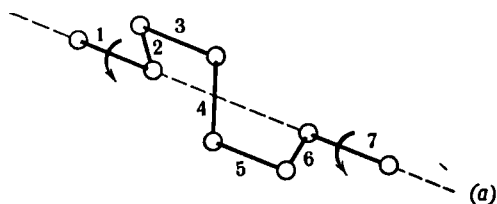


Fig. 5.4. The molecular mechanism of γ -relaxation—the movement of aliphatic carbon atoms of the crankshaft rotation type:

a—the Schatzki model; *b*—the Boyer model.

At lower temperatures there are observed dielectric loss peaks due to small kinetic units of main or side chains in polymers which consist of a sequence of several carbon atoms. Such loss peaks (γ -relaxation) are usually assigned to the movement of several CH_2 or CF_2 groups.

Another possible mechanism of both dielectric and mechanical relaxation (γ -relaxation) is the crankshaft rotation observed below the glass-transition temperature (Fig. 5.4). Schatzki (12) assumed that this mechanism leads to a relaxation process observed near -120°C in measurements at a frequency of about 1 Hz in polymers containing a linear sequence of methylene groups $(-\text{CH}_2-)_n$, where $n \geq 4$. This relaxation process, which has come to be known as the γ -relaxation, is observed in polyethylene, aliphatic polyamides and polyesters, and some polymethacrylates containing linear methylene chains in side branches.

The mechanism of molecular motion proposed by Schatzki is shown in Fig. 5.4. It consists of the simultaneous rotation of a segment of the polymeric chain about the bonds 1 and 7 in such a way that the carbon atoms contained in this chain unit move like a crankshaft. It is essential here that bonds 1 and 7 are collinear. The other parts of the chains or side groups may remain frozen, the motion taking place in only a relatively small volume. If all the valence angles and bond lengths are equal, then, according to Schatzki, four carbon atoms must be present between the collinear bonds. Boyer (13) conjectured that the chain unit that effects the hindered rotation associated with the transition from one conformation to another contains only two carbon atoms (see Fig. 5.4). This structure of the kinetic unit responsible for the γ -relaxation contains, however, an energetically less favourable *cis*-conformation about bond 3, and so seems less probable than the Schatzki model.

The possibility of this kind of movement (crankshaft rotation) in polymers containing aliphatic linkages is also pointed out by Wunderlich (14), who maintains that collinear bonds may in this case be separated by three carbon atoms. There is a large body of experimental data confirming the molecular mechanism of γ -relaxation based on crankshaft rotation. The presence in the polymeric chain of runs of three or more CH_2 units, each of which is linked to immobile groups, leads to the appearance of γ -relaxation in various polymers (1, 2). The available experimental data indicate that this mechanism is possible only in amorphous polymers or in amorphous regions of crystalline polymers. This is because the crankshaft rotation can only occur about two collinear bonds. This condition is not fulfilled in crystalline regions, where the sequences of methylene groups form mainly *trans*-conformations.

The activation energy of the γ -relaxation process observed in amorphous regions ranges from 50 to 63 kJ/mole, which is in good agreement with the values predicted by Schatzki (54 kJ/mole). His value for activation energy was obtained on the basis of the assumption that for the crankshaft rotation to be realized it is necessary that the potential barrier that exists in butane ($U = 31.4$ kJ/mole) and the potential barrier ($U = 21$ – 25 kJ/mole) calculated from the cohesive energy density be overcome. It is interesting that the predicted free volume required for this to occur is four times greater than the molar volume of the methylene group. This agrees well with estimates made on the basis of experimental investigations.

Despite the fact that, according to Boyer (13), the crankshaft rotation may prove to be the principal mechanism of a secondary (below T_g) relaxation in various polymers, no theory has been developed that could predict on the basis of this mechanism the peak intensity or width of a dielectric or mechanical relaxation.

Most theories of relaxation phenomena in polymers rest on the fundamental assumption of the possibility of the internal rotation of the individual elements of macromolecules about certain chemical bonds. Processes of this type are thermal-activation processes and involve the jump of atoms (or groups of atoms) over a potential-energy barrier from one equilibrium position to another. There are other quite different mechanisms which enable one to explain dielectric relaxation processes in polymers. Such mechanisms have been considered by Yamafuji and Ishida (15), Gotlib and Salikhov (16) and others (17). One of these mechanisms involves repressing the oscillations of units of the polymeric chain which occur near the equilibrium position. This relaxation mechanism is called the local mode. A mechanism of this kind was used by Hill (18) for calculating the dispersion of the dielectric constant in polar liquids.

Saito *et al.* (17) considered the oscillations of a molecule surrounded by other molecules about the position corresponding to its local

equilibrium conformation. The analysis rests on the assumption that the superposition of oscillations is a set of normal vibrations.

The characteristic frequency of the n th normal vibration is given by

$$\omega_n = \sqrt{c_n/m} \quad (5.49)$$

where c_n is the relevant force constant; m is the mass of the vibrating unit.

The expression for x_n (the mean square of the amplitude) of the n th vibration has the form:

$$\sqrt{\langle x_n^2 \rangle} = \left\{ \frac{2kT}{m\omega_n^2} \cdot \frac{\frac{\hbar\omega_n}{kT}}{e^{\frac{\hbar\omega_n}{kT}} - 1} \right\} \quad (5.50)$$

The characteristic frequencies and mean amplitudes have a rather wide distribution. Though the force constants for torsional vibrations are very small as compared with the force constants for other modes of vibration, torsional vibrations may be regarded as vibrational modes with the lowest frequency and the largest amplitude. It is evident that large-amplitude torsional vibrations will be strongly damped in the glassy state, which is characterized by a very high viscosity.

All this may lead to the occurrence of a relaxation process. Saito and his coworkers (17) carried out a detailed investigation of this relaxation process, introducing the friction ξ_l into the Kramers-Chandrasekhar diffusion equation. The relaxation time for local modes is defined as

$$\tau_\lambda = \xi_l / c_\lambda \gg 1/\omega_\lambda \quad (5.51)$$

where c_λ is the force constant for torsional vibration λ ; ω_λ is the corresponding natural frequency.

From expression (5.51) it follows that at large ξ the relaxation frequency τ_λ^{-1} will be much lower than the characteristic frequency of the original normal vibrations. The order of magnitude of the activation energy associated with the viscosity was estimated on the assumption that the moving group is surrounded by vacancies, the volume of which is larger than a certain critical value. The critical volume is calculated on the basis of the potential of intermolecular interaction in the form of the Lennard-Jones potential. The calculated value of the activation energy for the local modes is about 42 kJ/mole. It has been shown (17) that for this relaxation process the difference of the dielectric constants is given by

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi n N g p_0^2}{3c_\lambda} \left(\frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right) \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \quad (5.52)$$

where n is the number of dipole units in the chain; g is the correlation factor; p_0 is the dipole moment of the repeating unit.

Expressions for the difference $\varepsilon_0 - \varepsilon_\infty$ which are more exact and, hence, more complicated than formula (5.52) have been used to describe low-temperature relaxations caused by local modes in such polymers as polyvinyl chloride, polyethylene terephthalate and polyformaldehyde.

The theory of local modes is employed in a number of cases to account for some subsidiary relaxation processes and predicts correctly the level of dispersion in dielectric relaxation. Nonetheless, this theory, like other theories, relates the relaxation time to a certain viscosity coefficient which is very difficult to predict.

Relaxation processes that occur in polymers at very low temperatures have a quantum nature (1).

5.4. Dielectric Properties and Structure

5.4.1. Crystalline Polymers

The effect of the degree of crystallinity on the dielectric properties of polymers has been studied most extensively. Suppose that dielectric relaxation processes that occur in polymers may be regarded as a superposition of relaxation processes in fully crystalline and fully amorphous samples of the polymer. Then the expression for the dielectric relaxation-time spectrum density may be represented in the form:

$$H(\tau) = \kappa H_1(\tau) + (1 - \kappa) H_2(\tau) \quad (5.53)$$

where κ is the degree of crystallinity; the subscripts 1 and 2 refer to the completely crystallized and completely amorphous samples, respectively.

Substituting expression (5.53) into formulas (5.31) and (5.32) and assuming that ε_∞ is connected with κ by a relation of the type (5.53), we deduce formulas that establish the relationship between the dielectric properties of polymers and the degree of crystallinity:

$$\varepsilon' = \kappa \left(\varepsilon_{1\infty} + \int_0^\infty \frac{H_1(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + (1 - \kappa) \left[\varepsilon_2 + \int_0^\infty \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right] \quad (5.54)$$

$$\varepsilon'' = \kappa \int_0^\infty \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} + (1 - \kappa) \int_0^\infty \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \quad (5.55)$$

Let the second terms on the right-hand side of expressions (5.54) and (5.55) be substantially larger than the first. Then the terms containing the factor $(1 - \kappa)$ will make the major contribution to ε'

and ϵ'' . As a result, ϵ' and ϵ'' will decrease with increasing degree of crystallinity. Since the dependence of ϵ'' on κ is stronger than that of ϵ' , it follows that as the degree of crystallinity increases the dielectric loss tangent ($\tan \delta$) will also diminish.

Such a dependence of dielectric properties on the degree of crystallinity is usually observed at temperatures higher than the glass-transition temperature of amorphous regions. For example, some polyolefins are found to be in such a state at room temperature.

If we neglect the first term on the right-hand side of formula (5.54) as compared with the second, the expression for the dielectric constant will take the following form:

$$\epsilon' \approx (1 + \kappa) \left(\epsilon_{2\infty} + \int_0^\infty \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) \quad (5.56)$$

From expression (5.56) it follows that as the degree of crystallinity increases the quantity ϵ' diminishes. Relation (5.56) may be rewritten thus:

$$\epsilon' = \left(\epsilon_{2\infty} + \int_0^\infty \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + \frac{1}{\rho_1 - \rho_2} \left(\epsilon_{2\infty} + \int_0^\infty \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) (\rho_2 - \rho) \quad (5.57)$$

where ρ is the density of the polymer; the subscripts 1 and 2 refer, respectively, to the completely crystalline and completely amorphous samples of the same polymer.

If we assume that in polymers at temperatures higher than the glass-transition temperature of the amorphous regions, for all $\omega\tau$ that make the most significant contribution to the relaxation spectrum there is satisfied the condition $\omega\tau \ll 1$, then formula (5.57) will, at least qualitatively, repeat the well-known (7) empirical expression for polyolefins:

$$\epsilon' = 2.276 + 2.01 (0.92 - \rho) \quad (5.58)$$

From this it becomes clear with what assumptions the empirical formula (5.58) holds true.

The possibility is not excluded that with crystalline polymers there may also occur a case when the first term on the right-hand side of one of the formulas (5.54) or (5.55) by far exceeds the second. Then ϵ' and ϵ'' will increase with increasing degree of crystallinity. Such an increase in ϵ'' and $\tan \delta$ with increasing κ is really often observed. This is manifested especially prominently when the intensity of the relaxation peaks due to molecular mobility in the crystalline regions increases with increasing κ .

From formulas (5.54) and (5.55) there also emerges an interesting regularity: as the temperature is lowered (at $T \rightarrow 0$), when $\omega\tau \rightarrow \infty$,

the dielectric constant ϵ' is determined by the parameter ϵ_∞ alone. Since the values of ϵ_∞ for a number of non-polar (polyethylene, polytetrafluoroethylene) and polar (polyamides) crystalline polymers differ little, it is then obvious that at very low temperatures the dielectric constant of these polymers must be almost identical. We can then conclude that when the relaxation spectrum is "frozen" through a decrease in temperature much of the difference between polar and non-polar polymers will disappear (at least, as far as the value of ϵ' is concerned), and at $T \rightarrow 0$ a polar polymer must behave like a non-polar one. Such a dependence of ϵ' on temperature is really observed (1), which confirms the validity of formulas (5.31) and (5.54).

5.4.2. Network Amorphous Polymers

The main structural parameter of network polymers is the degree of cross-linking defined as:

$$\nu = \rho/M_c \quad (5.59)$$

where ρ is the density of the polymer; M_c is the molecular mass of the portion of the polymeric chain between two neighbouring network entanglement junctions.

By analogy with formula (5.53) the expression for the relaxation-time spectrum density of a network polymer may be written in the following form:

$$H(\tau) = \varphi H_1(\tau) + (1 - \varphi) H_2(\tau) \quad (5.60)$$

where the subscripts 1 and 2 refer, respectively, to the sample with a maximum degree of cross-linking and the sample devoid of chemical cross links, both samples belonging to the same polymer; $\varphi = \nu/\nu_m$; ν_m is the maximum possible degree of cross-linking for a given polymer.

Thus, φ is the relative space-network density. The parameter φ may vary from 0 (an uncross-linked polymer) to 1 (at $\nu = \nu_m$). Substituting expression (5.60) into formulas (5.31) and (5.32), we obtain formulas that establish the relationship between the dielectric properties and the degree of cross-linking:

$$\epsilon' = \varphi \left(\epsilon_{1\infty} + \int_0^\infty \frac{H_1(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + (1 - \varphi) \left(\epsilon_{2\infty} + \int_0^\infty \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) \quad (5.61)$$

$$\epsilon'' = \varphi \int_0^\infty \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} + (1 - \varphi) \int_0^\infty \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \quad (5.62)$$

Let us consider two special cases. Suppose that

$$\int_0^{\infty} \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \ll \int_0^{\infty} \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2}$$

Such a situation when the ϵ'' of an uncross-linked polymer is much higher than the ϵ'' of the same polymer but with a maximum degree of cross-linking does really occur if both polymers are in the rubbery state. In such a case the major contribution to ϵ'' will come from the second term on the right-hand side of formula (5.62), and the dielectric losses will diminish with increasing degree of cross-linking. This regularity manifests itself especially prominently in the region of transition of the network polymer from the glassy to the rubbery state. In such cases, as the value of φ increases there is observed a substantial decrease in the intensity of the principal relaxation peak (the α -peak) in the temperature dependence of ϵ'' or $\tan \delta$.

If we have

$$\int_0^{\infty} \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} > \int_0^{\infty} \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2}$$

then the first term will predominate in formula (5.62), and the dielectric losses will increase with increasing degree of cross-linking. Such a dependence can be observed in network polymers below the glass-transition temperature T_g in the region of a secondary (dipolar group) loss peak [for example, in cured epoxide resins (7)].

Evidently, in the glassy state a large degree of cross-linking reduces the effectiveness of the intermolecular interaction of the kinetic units of the neighbouring chains, thereby contributing to the increase of the intensity of molecular motion, which is what leads to an increase in ϵ'' and $\tan \delta$.

5.4.3. Dielectric Properties of Plasticized Polymers and Plasticizer Concentration

By analogy with relations (5.53) and (5.60) we can write:

$$H(\tau) = \xi H_1(\tau) + (1 - \xi) H_2(\tau) \quad (5.63)$$

where $\xi = k/k_m$ is the relative concentration of plasticizer; k_m is the maximum plasticizer concentration at which the plasticizer is compatible with the polymer; the subscripts 1 and 2 refer, respectively, to the sample with a maximum plasticizer concentration and the unplasticized sample of the same polymer.

Substituting expression (5.63) into formulas (5.31) and (5.32), we obtain:

$$\epsilon' = \xi \left(\epsilon_{1\infty} + \int_0^{\infty} \frac{H_1(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + (1 - \xi) \left(\epsilon_{2\infty} + \int_0^{\infty} \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) \quad (5.64)$$

$$\epsilon'' = \xi \int_0^{\infty} \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} + (1 - \xi) \int_0^{\infty} \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \quad (5.65)$$

If we have

$$\epsilon_{1\infty} + \int_0^{\infty} \frac{H_1(\tau) d\tau}{1 + \omega^2 \tau^2} \gg \epsilon_{2\infty} + \int_0^{\infty} \frac{H_2(\tau) d\tau}{1 + \omega^2 \tau^2}$$

then ϵ' will increase with increasing plasticizer concentration. Such a relationship between ϵ' and ξ is often observed upon addition of polar plasticizers to polymers. Usually, as the concentration of the polar plasticizer introduced into a polar polymer is increased, the intensity of the principal relaxation peak in the temperature dependence of ϵ'' diminishes. This is accompanied by a decrease in the relaxation times corresponding to the vitrification process, which leads to the shift of the α -peak on the $\epsilon'' = f(T)$ graph to lower temperatures. This is an indication that the following condition is satisfied:

$$\int_0^{\infty} \frac{H_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} > \int_0^{\infty} \frac{H_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \quad (5.66)$$

In this case, from formula (5.65) it follows that as the plasticizer concentration is increased the dielectric losses in the plasticized polymer must diminish.

Inequality (5.66) is also fulfilled in those cases when plasticized polymers are in the glassy state. Here the dielectric losses (ϵ'' and $\tan \delta$) decrease with increasing plasticizer concentration. This applies also to the variation of the intensity of the β -peaks and is one of the criteria of "anti-plasticization", the special features of which are sufficiently clear at present (2).

Indeed, the enhancement of the effectiveness of the intermolecular interaction in an "anti-plasticized" polymers below T_g must lead to the suppression of molecular motion. The result is a decrease in the intensity of the secondary loss peak in a polar polymer plasticized by a polar plasticizer.

Such a decrease in ϵ''_m has been observed in plasticized polyvinyl chloride (19, 20). It has been found that with a plasticizer content higher than 20 per cent the secondary (dipolar-group) loss peak in polyvinyl chloride is completely repressed.

Mikhailov and coworkers (19) have shown that a decrease in the intensity of the β -process in plasticized polyvinyl chloride is associated with an increase in the probability of formation of more rigid chain conformations. Other investigators (20) attribute this effect to a change in the supermolecular structure of polyvinyl chloride that takes place during plasticization. It has been established (2) that both these viewpoints reflect the different aspects of one and the same physical phenomenon—"antiplasticization".

References

1. Perepechko, I. I., *Low-Temperature Properties of Polymers*, Mir Publishers, Moscow and Pergamon Press, Oxford, 1980.
2. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers, Moscow, 1975.
3. Debye, P., *Polar Molecules*, Dover, New York, 1945.
4. McCrum, N. G., B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
5. Brown, W. Jr., *Dielectrics*, Berlin, 1956.
6. Frölich, H., *Theory of Dielectrics*, Oxford University Press, Oxford, 1949.
7. *Electrical Properties of Polymers*, ed. by B. I. Sazhin, Khimiya, Leningrad, 1970 (in Russian).
8. *Dielectric Properties of Polymers*, ed. by F. E. Karasz, Plenum Press, New York, 1972.
9. Cole, R. H., in: *Progress in Dielectrics*, ed. by J. B. Birks, vol. 3, Heywood, London, 1961.
10. Meakins, R. J., in: *Progress in Dielectrics*, ed. by J. B. Birks, vol. 3, Heywood, London, 1961.
11. Bartenev, G. M. and Yu. V. Zelenev, *Mekhanika Polimerov*, 1, 30 (1969).
12. Schatzki, T. F., *Am. Chem. Soc. Polymer Preprints*, 6, 2, 646 (1965).
13. Boyer, R. F., *Rubb. Chem. Technol.*, 36, 1303 (1963).
14. Wunderlich, B., *J. Chem. Phys.*, 7, 10, 2429 (1962).
15. Yamafuji, K. and Y. Ishida, *Koll.-Z.*, 183, 1, 15 (1962).
16. Gotlib, Yu. Ya., and K. M. Salikhov, *Vysokomol. Soedin.*, 4, 8, 1163 (1962).
17. Saito, N. *et al.*, in: *Solid State Physics*, vol. 14, Academic Press, New York, 1963.
18. Hill, N. E., *Proc. Phys. Soc.*, 82, 5, 529, 723 (1963).
19. Mikhailov, G. P., A. M. Lobanov, and D. M. Mirkamilov, *Vysokomol. Soedin.*, 8, 8, 1352 (1966).
20. Lebedev, V. P., L. E. Derlyukova, I. N. Razinskaya, I. L. Okladnov, and B. P. Shtarkman, *Vysokomol. Soedin.*, 7, 2, 333 (1965).

Chapter 6

Nuclear Magnetic Resonance

6.1. Basic Concepts of Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a phenomenon caused by resonance transitions between the magnetic energy levels of atomic nuclei in an external field. Basic information on nuclear magnetic resonance can be found in a number of monographs (1-5) and review articles (6-10). We shall recall only the most important principles. It is well known that the nuclei of many isotopes have not only mass and charge but also a momentum. The intrinsic angular momentum of nuclei is called the spin. The presence of a spin in a nucleus leads to the existence of an intrinsic magnetic moment. In this book we shall speak mainly of the nuclei of the hydrogen atom—protons. The intrinsic magnetic moment of a proton is very small as compared with that of an electron and manifests itself only in special physical experiments.

In a number of cases, we can consider, at a first approximation, a system of isolated atomic nuclei placed in an external magnetic field. Obviously, the magnetic moment of an isolated proton in an external magnetic field can have two possible directions: parallel or antiparallel to the applied field. To each of these directions of the magnetic moment of the proton there correspond specific energy levels of the proton. The difference between the energies corresponding to these energy levels can be given in the form:

$$\Delta E = 2\mu H_0 \quad (6.1)$$

where μ is the magnetic moment; H_0 is the strength of the applied external field.

In accordance with the laws of quantum mechanics, the transition of the nucleus (proton) from one energy level to another is associated with the absorption or emission of a quantum of energy $h\nu$. It then follows that

$$h\nu = 2\mu H_0 \quad (6.2)$$

Thus, if an electromagnetic wave of frequency ν is propagating in a substance whose nuclei have a magnetic moment μ and which is placed in an external magnetic field H_0 , then with condition (6.2) being fulfilled the absorption of energy is possible. As a result, the

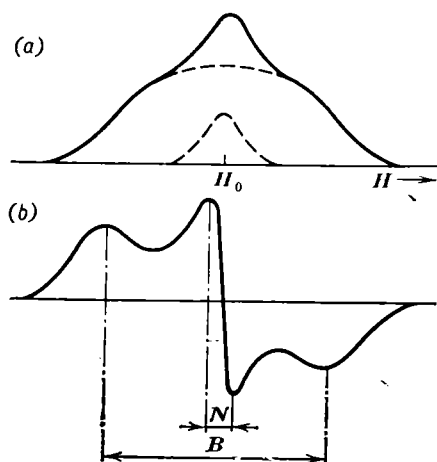


Fig. 6.1. The superposition of two NMR spectra:

a—resonance absorption curves (the solid line is the integral curve, and the dashed lines represent its components); *b*—the first derivative with respect to the magnetic field strength (N is the width of the narrow component, and B is the width of the broad component).

atomic nuclei can jump to another, higher energy level corresponding to another orientation of their intrinsic magnetic moment and momentum. If the substance (a polymer) is placed between the poles of a magnet producing an external field of strength $H_0 = 10^4$ gauss then the proton absorbs or emits electromagnetic energy of frequency $\nu = 42.57$ MHz. The phenomenon of nuclear magnetic resonance is precisely the absorption or emission of the energy of electromagnetic high-frequency oscillations when a substance is placed in a magnetic field.

In the very crude approximation given above, the absorption spectrum of the proton will constitute a single line. In fact, each proton of the polymer is also influenced by the magnetic fields of the surrounding protons. This leads to the appearance of a non-zero local magnetic field strength H_{loc} due to the magnetic moments of the neighbouring protons. The local field can either oppose or augment the magnetic field acting on the proton, depending on the orientation of the magnetic moments of the interacting protons. If we take account of the local field, the resonance condition (6.2) must be written in the form

$$h\nu = 2\mu(H_0 + H_{loc}) \quad (6.3)$$

The presence of a local field leads to the splitting of the energy levels and to the smearing-out of the absorption spectrum in resonance. The local field strength is not great: it is equal to 5-10 gauss with the external field strength H_0 being approximately equal to 10^4 gauss. Nevertheless, by virtue of the very large number of interacting protons (and also of isolated groups of protons) the local field leads to the appearance of an absorption spectrum with a complex shape and a finite half-width.

The experimental observation of nuclear magnetic resonance is usually conducted so that the frequency ν of the electromagnetic

wave propagating in a polymer remains constant (it is equal to several tens of MHz), while the magnetic field strength H_0 varies smoothly within the relatively narrow limits sufficient for the resonance condition (6.3) to be fulfilled. In a general case, the resonance absorption curve can have a complex form (Fig. 6.1). It is not the absorption curve that is most often recorded but its first derivative with respect to the magnetic field strength (Fig. 6.1).

6.1.1. The Lineshape of the NMR Signal

The NMR signal lineshape in polymers depends on the chemical and physical structure and the physical state of the polymer. In the case of amorphous polymers the presence of a local field and a strong intermolecular interaction gives a sufficiently broad absorption curve for such polymers in the glassy state. As the temperature rises the molecular mobility increases and the atoms (and, hence, their nuclei) begin to participate in this motion. This results in a certain time-averaging of the local field and, hence, to a decrease in it. The decrease in H_{loc} leads, in turn, to the narrowing of the resonance absorption curve. When the rubbery state is attained (this state being characterized by an intensive molecular motion), the absorption curve becomes very narrow as compared with the corresponding curve for the glassy state.

In the case of crystalline polymers at temperatures above the glass-transition temperature of the amorphous layer the lineshape of the NMR signal is found to be more complicated. In this case the spectrum consists of two parts: a broad component corresponding to processes taking place in the crystalline regions, and a narrow component due to segmental mobility in the amorphous regions.

The main parameters characterizing the NMR lineshape are the linewidth δH and the second moment ΔH^2 . These parameters can in a number of cases be calculated theoretically.

6.1.1.1. Linewidth

The linewidth δH of the NMR spectrum is the distance between the two points on the absorption curve at which the amplitude of the signal decreases by a factor of 2. Since it is usually the first derivative of the absorption curve with respect to the field strength which is written out, the linewidth is sometimes defined as the distance between the two points on the absorption curve at which the shape of the curve changes most. In the latter case, δH is defined as the distance between the corresponding extrema of the real NMR spectrum. In the case of crystalline polymers, one sometimes speaks of the width of the narrow and broad components of the spectrum. The linewidth is often measured as the distance between the outer maximum and minimum (see Fig. 6.1).

6.1.2. The Second Moment of the NMR Spectrum

A theoretical description of the shape of the NMR spectrum line is a very complicated task. However, it is possible in a number of cases to calculate sufficiently accurately the integral characteristic of the resonance absorption curve—the second moment of the resonance line contour. According to the van Vleck theory (11), the second moment ΔH_2^2 is defined by the expression

$$\Delta H_2^2 = \frac{\int_{-\infty}^{\infty} f(H) (H - H_0)^2 dH}{\int_{-\infty}^{\infty} f(H) dH} \quad (6.4)$$

where $f(H)$ is the magnetic field strength function characterizing the lineshape; $(H - H_0)$ is the amount by which the field differs from the resonance value (the coordinate being taken from the centre of the spectral line).

In the denominator of expression (6.4) there is an integral introduced for normalization. Thus, the second moment of the NMR spectrum line may be regarded as a linewidth which is determined according to some special method and averaged; it is expressed in units of the magnetic field strength and is calculated from experimental curves. Since the first derivative of the resonance line $\varphi(H)$ is usually determined, the quantity ΔH_2^2 can be given in the following form:

$$\Delta H_2^2 = \frac{1}{3} \cdot \frac{\int_{-\infty}^{\infty} (H - H_0)^3 \varphi(H) dH}{\int_{-\infty}^{\infty} (H - H_0) \varphi(H) dH} \quad (6.5)$$

The expression for ΔH_2^2 can be calculated theoretically as a function of the magnitude and orientation of the internuclear vectors with respect to the applied external field. In this connection, it is possible, with the structural model being specified, to calculate ΔH_2^2 theoretically and, comparing it with experimental values, to come to some conclusions as to how reliably the model describes the actual structure.

Like the linewidth, the second moment will decrease with increasing temperature. The strong decrease in ΔH_2^2 with increasing temperature allows us to establish the temperature regions in which the various modes of molecular motion are unfrozen. The strongest decrease in ΔH_2^2 in amorphous polymers is observed on transition from the glassy to the rubbery state.

6.1.2.1. Correlation Frequency and Energy of Activation

It has already been mentioned above that δH and, hence, ΔH^2 depend on the strength of the local field H_{loc} that acts on each nucleus. If the atomic nuclei are involved in thermal motion, the local field strength is a function of time. Thus the parameters that characterize the average value of $\langle H_{\text{loc}}^2(t) \rangle$ and the rate of variation of this quantity are of greatest interest. In order to describe the time-averaged value of H_{loc}^2 , use is made of the concept of the correlation function:

$$R(t) = \langle H_{\text{loc}}(t) \cdot H_{\text{loc}}(t + \tau) \rangle \quad (6.6)$$

From expression (6.6) it follows that the correlation function in this particular case is the time-averaged value of the product of the strengths of the local fields separated by the time interval τ . In our case, the correlation function is a measure of the connection between two successive values of $H_{\text{loc}}(t)$. In this way we can introduce the concept of the correlation time τ_c , which is a parameter that characterizes the rate of variation of the local field with time and, hence, the rate of variation of the correlation function. If $\tau = \tau_c$, then the value of the correlation function $R(t)$ defined by Eq. (6.6) decreases by a factor of e . The correlation time is, to a certain extent, analogous to the dielectric relaxation time. This analogy becomes especially complete when we are dealing with liquids. The correlation time τ_c in this case is connected by a simple relation with the dielectric relaxation time τ_D , found from the formula which follows from the Debye theory:

$$\tau_c = \tau_D/3$$

The dielectric relaxation time τ_D characterizes the rotation of molecules due to thermal motion, which leads to the disorientation of electric dipoles after the electric field is removed; this motion is considered with respect to the fixed coordinate system. The correlation time τ_c determines the rate of variation of the local field with respect to the nucleus involved in thermal motion. Hence, τ_c characterizes the change in the local field relative to the fixed coordinate system rigidly connected with the moving nucleus.

By analogy with relaxation-time spectra, one can also speak of correlation-time spectra. This is especially important when dealing with NMR in polymers. If the process associated with the unfreezing of some mode of molecular motion can be described with the aid of a single "effective", average correlation time, then the inverse of this time, $1/\tau_c = 2\pi\nu_c$, can be calculated from experimental data:

$$2\pi\nu_c = \frac{\alpha\gamma\delta H}{\tan\left(\frac{\pi}{2} \cdot \frac{\delta H^2 - B^2}{C^2}\right)} \quad (6.7)$$

where ν_c is the correlation frequency for a molecular motion leading to the narrowing of the resonance curve; α is a constant equal to 0.18; γ is the gyromagnetic ratio equal to the ratio of the magnetic moment to the momentum; δH is the linewidth over a temperature range in which a given mode of molecular motion is unfrozen [δH is the convected coordinate in Eq. (6.7)]; B is the linewidth at a temperature lying above the transition region; C is the linewidth at a temperature at which a given mode of motion is still "frozen".

Having determined the linewidth δH at several temperatures in the transition region, one can calculate, by means of Eq. (6.7), the average correlation frequency at several temperatures and then calculate the activation energy of the process under study using the formula

$$\nu_c = \nu_\infty e^{-\frac{U}{RT}} \quad (6.8)$$

6.1.3. The Spin-Lattice Relaxation Time

Two methods are possible for investigating NMR in polymers. One method consists of treating a given volume of the polymer, which is in effect a set of macromolecules, as a certain "lattice". In this case, the lattice can be described not only as an ordered arrangement of chains in crystallites but also as a certain order ("short-range order") in amorphous polymers or in the amorphous regions of crystalline polymers. In the second method, one speaks of the ordering due to the orientation of magnetic dipoles, which is governed by the presence of nuclear spins.

Thus, a polymer can be looked upon as a combination of two systems: a lattice and a system of spins. These systems interact weakly since the magnetic dipoles (the nuclear magnetic moments) usually interact much more strongly with the external magnetic field produced by the magnet in an NMR experiment than between one another ($H_0 \gg H_{loc}$). The polarization of the nuclear magnetic moments upon application of an external magnetic field exerts a decisive influence on the orientation of spins in a polymeric material, with the thermal motion of atoms affecting the ordering in the arrangement of spins only slightly. If a magnetic field is applied to a polymeric material which has nuclear magnetic moments and is then removed, the magnetic polarization of nuclei will begin to decay because of the thermal motion. The phenomenon of spin-lattice relaxation is a spontaneous decay of magnetic polarization in the absence of an external magnetic field, caused by the thermal motion of atoms.

In spite of the fact that the characteristic times of thermal motion in polymers are sufficiently shorter, and do not exceed 10^{-5} - 10^{-10} s, the spin-lattice relaxation time T_1 is usually long and equals several seconds or minutes. The cause of this is the weak interaction between

the spin system and the lattice. It might seem that the thermal motion of atoms should alter the interaction between the nuclear magnetic moments sufficiently rapidly, but by virtue of the fact that the energy of such interaction is much lower than the total energy of the magnetic dipoles that have been polarized by the external magnetic field, the elements of the polymeric chains must undergo repeated re-orientations before the overall magnetic interaction is appreciably reduced. The decay of the magnetization vector (caused by the orientation of the nuclear magnetic moments) is a process of transition to equilibrium between the spin system and the lattice.

The spin-lattice relaxation associated with molecular motion is most distinctly observed when the frequency of thermal vibrations is comparable with the NMR frequency. Therefore, the investigation of spin-lattice relaxation is carried out at frequencies of the order of 10^6 to 10^8 Hz. If measurements are made at a fixed frequency over a sufficiently wide temperature range, it turns out that the spin-lattice relaxation time passes through a minimum that appears at a quite definite temperature for each relaxation process. These minima are, to a certain extent, analogous to the maxima of the temperature dependence of dielectric losses.

The theory of the phenomenon of nuclear spin-lattice relaxation has been worked out by Bloembergen, Purcell and Pound (12), who derived a formula for the longitudinal spin-lattice relaxation time which takes account of a single correlation time τ_c . Since polymers have a wide range of correlation times, the expression for the longitudinal spin-lattice relaxation time T_1 can be given in the following form (13):

$$\frac{1}{T_1} = \frac{2}{3} (\Delta H_2^2) \left[\int_0^\infty \frac{I(\tau_c) \tau_c d\tau_c}{1 + \omega^2 \tau_c^2} + 4 \int_0^\infty \frac{I(\tau_c) \tau_c d\tau_c}{1 + 4\omega^2 \tau_c^2} \right] \quad (6.9)$$

where ΔH_2^2 is the second moment; $I(\tau_c)$ is the correlation time spectrum density (the relaxation-time distribution function).

6.2. Effect of Structure on Nuclear Magnetic Resonance

6.2.1. Effect of Crystallinity on the NMR Linewidth

Maklakov and Grigoriev have shown (14) that the expression for the linewidth δH in the presence of a correlation-time spectrum may be given in the form:

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \int_0^\infty \frac{I(\tau_c) \omega_0 \tau_c d\tau_c}{1 + \omega_0^2 \tau_c^2} \quad (6.10)$$

where δH_T is the width of the NMR absorption line for the rigid lattice; $\omega_0 = \alpha\gamma\delta H$ is a parameter with the dimensionality of cyclic frequency; a is a constant of the order of unity; γ is the gyromagnetic ratio.

It might seem at first glance that it follows from Eq. (6.10) that at $\omega_0\tau_c \rightarrow \infty$ (the region of very low temperatures) $(\delta H)^2 \rightarrow 0$. In actual fact, this is not so since $I(\tau_c)$ is a function of $\omega_0\tau_c$. It can be shown that $I(\tau_c) = \omega_0\tau_c \bar{I}(\tau_c)$. Substituting this expression into Eq. (6.10), we get:

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \int_0^\infty \frac{\bar{I}(\tau_c) \omega_0^2 \tau_c^2 d\tau_c}{1 + \omega_0^2 \tau_c^2} \quad (6.11)$$

It can be seen that at $\omega_0\tau_c \rightarrow \infty$ the quantity $(\delta H)^2$ assumes a finite value, increasing with increasing $\omega_0\tau_c$. Maklakov and Grigoriev (15) calculated theoretically the value of $\delta H/\delta H_T$ and demonstrated that it increases with an increase in $\omega_0\tau_c$, approaching a constant value:

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \int_0^\infty \bar{I}(\tau_c) d\tau_c \quad (6.12)$$

Following Chujo (16), we assume that the correlation-time spectrum density of an amorphous-crystalline polymer, $I(\tau_c)$, can be represented in the form of a linear superposition of the correlation-time spectra of crystalline, $I_{cr}(\tau_c)$, and amorphous, $I_{am}(\tau_c)$, regions:

$$I(\tau_c) = \kappa I_{cr}(\tau_c) + (1 - \kappa) I_{am}(\tau_c) \quad (6.13)$$

where κ is the "static" degree of crystallinity.

Chujo attempted to take account of the effect of crystallinity on the lineshape of the NMR signal in polymers by substituting expression (6.13) into the equation for the NMR absorption spectrum line contour derived by Mijake (13). He assumed, however, that all the correlation times corresponding to the crystalline regions are very long as compared with the τ_c of the amorphous regions. In view of this, Chujo disregarded the terms that contained the function $I_{cr}(\tau_c)$.

The Chujo assumption seems to be more or less justifiable only in those cases where the polymer is at a temperature exceeding the glass-transition temperature of the amorphous layer. At low temperatures, however, when the amorphous regions of a partly crystalline polymer are in the glassy state, the assumption could well prove to be invalid.

Substitution of expression (6.13) into Eq. (6.10) gives the dependence of the linewidth on the degree of crystallinity free from the

assumptions made by Chujo:

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \left[\kappa \int_0^\infty \frac{I_{cr}(\tau_c) \omega_0 \tau_c d\tau_c}{1 + \omega_0^2 \tau_c^2} + (1 - \kappa) \int_0^\infty \frac{I_{am}(\tau_c) \omega_0 \tau_c d\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \quad (6.14)$$

Analysis of Eq. (6.14) shows that two different forms of the dependence of the NMR linewidth on the degree of crystallinity are possible.

The nature of this dependence is determined by the relation between the integrals on the right-hand side of Eq. (6.14).

It is customarily believed that as the degree of crystallinity increases the total linewidth of a partly crystalline polymer also increases. Analysis of Eq. (6.14) indicates that this dependence is possible if the major contribution to $(\delta H)^2$ comes from the first integral on the right-hand side of formula (6.14). This condition is valid when the polymer is at a temperature higher than the T_g of the amorphous layer. One would be right in expecting that in this case $I_{cr}(\tau_c)$ will also be greater than $I_{am}(\tau_c)$, since the local field is time-averaged as a result of the intensive segmental motion in the amorphous regions above T_g . It is this form of the dependence of δH on κ that is the most widespread.

The main contribution to δH may, however, also come from the second integral on the right-hand side of Eq. (6.14). This is evidently possible only at a temperature lower than the glass-transition temperature of the amorphous layer, i.e., at low temperatures. One would expect $I_{am}(\tau_c)$ to be greater than $I_{cr}(\tau_c)$. If these conditions are fulfilled, the linewidth of the NMR signal will decrease with increasing degree of crystallinity. Inspection of Eq. (6.14) shows that in samples of the same polymer with different degrees of crystallinity, the linewidth can diminish with increasing κ at low temperatures (below T_g of the amorphous layer) and increase at relatively high temperatures (above T_g of the amorphous layer but below T_m of the crystallites). Thus, in certain polymers there is possible an inversion of the temperature dependence of the linewidth for samples of the same polymers which have different degrees of crystallinity. It is evident that the inversion region must lie near T_g of the amorphous layer measured at a corresponding frequency. When the temperature and the degree of crystallinity are changed, the correlation-time distribution function will also change. Maklakov and Grigoriev have shown (14-15) that when the distribution function of correlation times is changed on the graph of $\delta H/\delta H_T$ against $\omega_0 \tau_c$ the curves calculated theoretically for different widths of the correlation-time distribution will undergo inversion. It has been shown that the point of inversion is located at values of $\omega_0 \tau_c$ close to unity, which corresponds to the intensive manifestation of the relaxation

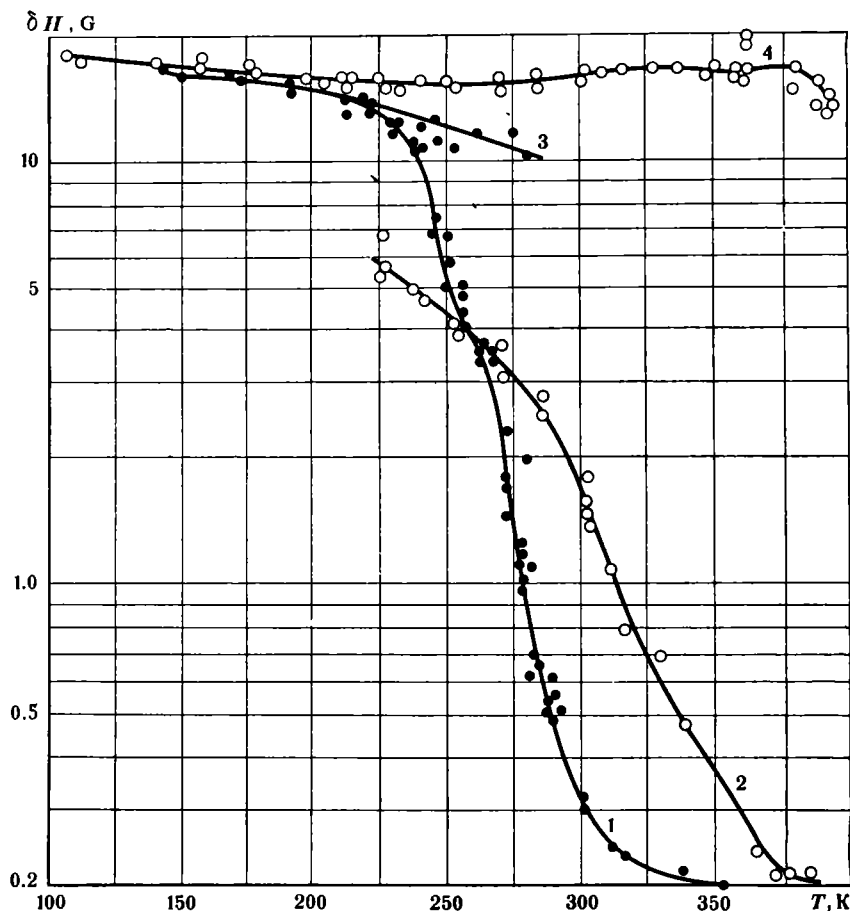


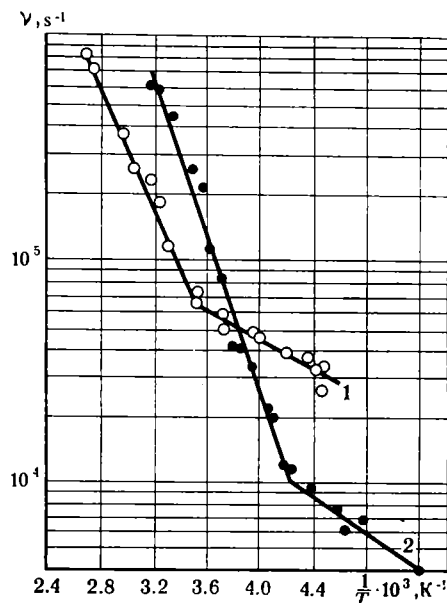
Fig. 6.2. The linewidths of the narrow (1, 2) and broad (3, 4) components of the NMR signal for polyethylene of low (1, 3) and high (2, 4) density.

process. Thus, the results of the analysis of Eq. (6.14) are in good agreement with the theoretical calculations of δH carried out by Maklakov and Grigoriev (14-15).

McCall and Slichter (17), while investigating low-density ($\kappa \approx 70$ per cent) and high-density ($\kappa \approx 50$ per cent) polyethylene, found that at low temperatures the width of the narrow component (which corresponds to the amorphous regions) in the less crystallized and more strongly branched polymer is much greater than the δH of the narrow component of the more crystallized linear polyethylene (Fig. 6.2). At high temperatures the situation is reversed and δH is greater for low-density polyethylene. It is interesting that the point of inversion on the $\delta H = f(T)$ graph for both polyethylenes is located at -20°C , which agrees well with the glass-transition temperature of the amorphous regions of polyethylene at frequencies of

Fig. 6.3. Dependence of the mean correlation frequency on inverse temperature:

1—high-density polyethylene; 2—low-density polyethylene.



about 10^4 Hz. It might seem at first sight incorrect to compare the values of δH for low-density and high-density polyethylenes for the purpose of estimating the effect of crystallinity, since not only their degrees of crystallinity are different but one of them is practically a linear polymer and the other has methyl groups as branchings. The presence of methyl groups in branched polyethylene, which, as will be shown at a later time, retain their mobility down to 0 K, must, however, reduce the δH of the narrow component, while at low temperatures δH for branched polyethylene turns out to be greater than for linear polyethylene. The average correlation frequency ν_c for low-density polyethylene at low temperatures is substantially lower (τ_c is greater) than in the case of high-density polyethylene (Fig. 6.3), despite the commonly held belief to the contrary.

The results obtained by means of the NMR method agree well with the temperature dependence of Young's dynamic modulus for these polymers (18). It has been shown experimentally that at low temperatures Young's dynamic modulus and the velocity of sound in the less crystallized high-density polyethylene exceed the corresponding values for the more strongly crystallized linear polyethylene. It has been shown (18) that the anomalous effect of crystallinity on the elastic modulus and the velocity of sound (at which these parameters decrease with increasing κ) is associated with the change in the effectiveness of intermolecular interaction in the amorphous regions and is typical of crystalline polymers for which the Hoseman-Bonart structural model is valid. If this analogy between the effect of κ on acoustical properties and the NMR linewidth at low temper-

atures is correct, one may then expect the results similar to those given in Fig. 6.3 to be obtained at low temperatures for polyethylene terephthalate, polycapramide, polyamide 68.

An analogous increase in the second moment below the glass-transition temperature T_g in amorphous samples of polyarylates as compared with crystalline samples has been really observed (19).

6.2.2. Effect of Degree of Cross-Linking on NMR Linewidth

One of the most important characteristics of amorphous network polymers is the degree of cross-linking:

$$\nu = \rho/M_c = N_c/N_0$$

where ρ is the density; M_c is the molecular mass of the portion of the chain between two entanglement points of the space network; N_c is the number of network chains per unit volume; N_0 is Avogadro's number.

The network chain is usually defined as the portion of the polymeric chain that connects the neighbouring entanglement junctions. Thus, the degree of cross linking (the network density) shows the number of moles of network chains per unit volume of the polymer.

For each network polymer there exists a maximum possible degree of cross-linking, ν_m , which depends on the chemical structure and the content of reactive groups. One may therefore speak of the relative degree of cross-linking $\phi = \nu/\nu_m$, where ν is the degree of cross-linking in the polymer. Obviously, ϕ varies from 0 (an uncross-linked polymer) to 1 (a polymer with the densest space network).

Let us consider the effect of the space network density ϕ on the NMR linewidth δH . To this end, we assume that the correlation-time spectrum density is given by

$$I(\tau_c) = \phi I_1(\tau_c) + (1 - \phi) I_2(\tau_c) \quad (6.15)$$

where $I_1(\tau_c)$ is the correlation-time spectrum density in a polymer having a maximum possible degree of cross-linking; $I_2(\tau_c)$ is the correlation-time spectrum density in a polymer which has the same chemical structure but has no chemical cross-links.

Substituting expression (6.15) into Eq. (6.11), we have

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \left[\phi \int_0^\infty \frac{I_1(\tau_c) \omega_0^2 \tau_c^2 d\tau_c}{1 + \omega_0^2 \tau_c^2} + (1 - \phi) \int_0^\infty \frac{I_2(\tau_c) \omega_0^2 \tau_c^2 d\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \quad (6.16)$$

Formula (6.16) allows one to account, at least qualitatively, for the dependence of δH on the network density at high temperatures and to predict it for low temperatures.

From formula (6.16) it follows that two kinds of dependence of the linewidth on φ are possible. If the predominant contribution to δH is made by the first integral on the right-hand side, then the linewidth increases with increasing network density. This kind of dependence of δH on φ must always be valid at $T > T_g$; it has been described in detail in the literature (1). It should be noted that this dependence can also be observed in the glassy state.

Another case is also possible: when $I_2(\tau_c) > I_1(\tau_c)$ and the linewidth is determined by the second term on the right-hand side of Eq. (6.16). In this case, the linewidth must decrease with increasing network density. This kind of dependence of δH on the degree of cross-linking can be expected to be valid in network polymers at low temperatures (at least, below T_g). Such an anomalous decrease in the linewidth at low temperatures must evidently be associated with the fact that the increase in the number of chemical cross-links will hinder the decrease in the distance between the kinetic units of the neighbouring chains with decreasing temperature of the polymer, thereby reducing the effectiveness of intermolecular interaction. As a result, the localized molecular mobility in polymers with a larger φ below T_g will be more intensive than in a slightly cross-linked polymer.

Such a change in molecular mobility in network polymers below T_g has been repeatedly observed (18). In network polymers such as cured epoxide resins and copolymers of unsaturated polyesters with styrene, the mechanical loss peaks, which are due to molecular mobility and are situated below the glass-transition temperature, increase with increasing network density. In investigating such polymers by the NMR method at low temperatures one may expect the increase in molecular mobility (of the non-segmental type) in the glassy state with increasing φ to lead to a decrease in the local magnetic field and, hence, to a decrease in the linewidth δH of the NMR signal.

It may be asserted that for network polymers the δH values of which at low temperatures (below T_g) decrease with a rise in φ the corresponding values will increase at high temperatures (above T_g) with increasing φ . It is natural that the second moment must vary, depending on φ in a manner analogous to the change in δH . Such different dependences of ΔH^2 on the degree of cross-linking above and below T_g have, it seems, been observed by Fujiwara and his coworkers (20) for polyethylene irradiated with an intensive beam of deuterons speeded up in an accelerator (Fig. 6.4). It is interesting that above 300 K (above T_g of the amorphous layer) the second moment for strongly irradiated (and, evidently, cross-linked) polyethylene is higher than in the case of an unirradiated polymer. This is sufficiently convincing evidence that the irradiation of polyethylene has produced cross-linking. Below 300 K the ΔH^2 value for

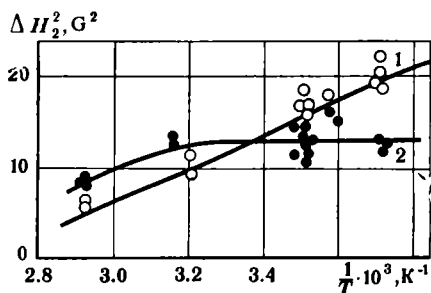


Fig. 6.4. Dependence of the second moment of the NMR signal on inverse temperature:

1—unirradiated polyethylene; 2—polyethylene irradiated with a beam of deuterons.

irradiated, radiation-cross-linked polyethylene is lower than for the unirradiated polymer. With a fall in temperature this difference increases (see Fig. 6.4).

6.2.3. Effect of Plasticizer Concentration on the NMR Linewidth

Let us examine the manner in which the concentration of a polar plasticizer added to a polar polymer influences the NMR linewidth δH .

Suppose that the polar polymer and the polar plasticizer added to it are compatible over a certain range of concentrations (the possibility of unlimited compatibility is not excluded). Let the plasticizer concentration in the polymer be k and the maximum permissible plasticizer concentration at which the plasticizer is still compatible with the polymer be k_m . We introduce the dimensionless parameter $\xi = k/k_m$.

It is evident that ξ may vary from 0 (an unplasticized polymer) to 1 (a polymer with a maximum possible plasticizer concentration). Hence, the parameter ξ indicates the degree of plasticization of the polymer.

Suppose that the correlation-time spectrum of a plasticized polymer, $\bar{I}(\tau_c)$, is represented as a linear superposition of the spectra of the infinitely plasticized polymer, $\bar{I}_1(\tau_c)$, and the unplasticized polymer, $\bar{I}_2(\tau_c)$, which have the same chemical structure. Then

$$\bar{I}(\tau_c) = \xi \bar{I}_1(\tau_c) + (1 - \xi) \bar{I}_2(\tau_c) \quad (6.17)$$

Substitution of expression (6.17) into Eq. (6.11) yields:

$$(\delta H)^2 = \frac{(\delta H_T)^2}{\pi} \left[\xi \int_0^\infty \frac{\bar{I}_1(\tau_c) \omega_0^2 \tau_c^2 d\tau_c}{1 + \omega_0^2 \tau_c^2} + (1 - \xi) \int_0^\infty \frac{\bar{I}_2(\tau_c) \omega_0^2 \tau_c^2 d\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \quad (6.18)$$

Inspection of this formula shows that in the region of the rubbery state, when for all τ_c that make a major contribution to the correlation-time spectrum the condition $\omega \tau_c \ll 1$ and $I_2(\tau_c) > I_1(\tau_c)$ is

fulfilled, the dominant contribution to the linewidth will be introduced by the second term on the right-hand side of expression (6.17). This means that the linewidth δH will diminish with increasing plasticizer concentration. This form of the dependence of δH on ξ is well known (1) and is very frequently encountered.

It is possible that $I_1(\tau_c) > I_2(\tau_c)$ and the major contribution to δH is made by the first term on the right-hand side of expression (6.17). In this case, the linewidth will increase with increasing plasticizer content in the polymer. This condition can be realized only for polymers in the glassy state and only in those cases where the addition of plasticizer to the polymer intensifies the intermolecular interaction in the polymer-plasticizer system below T_g , i.e., at low temperatures.

The intensification of intermolecular interaction in plasticized polymers leads to the suppression of molecular motion (18), which causes the broadening of the NMR line in plasticized polymers at low temperatures. Note that such an "anomalous" dependence of δH on ξ , when δH increases with increasing ξ if the polymer-plasticizer system is at a temperature below T_g , is a reflection of the effect of antiplasticization.

Antiplasticization has been thoroughly studied by acoustical methods (18). It means that upon addition of a polar plasticizer to a polar polymer the elastic modulus and the velocity of sound (and sometimes the strength too) in the polymer-plasticizer system at low temperatures (below T_g) increase with increasing plasticizer concentration. It has been found that antiplasticization is caused by an increase in the intermolecular interaction in the polymer-plasticizer system in the glassy state. The macroscopic manifestation of this effect consists of an increase in the elastic modulus and the velocity of sound with increasing ξ (δH behaves in an analogous manner in NMR) and a sharp decrease in the mechanical loss peaks situated below T_g .

It has been shown experimentally that upon addition of some low-molecular-mass liquids (acetic acid, ethyl alcohol) to Nylon 6,6 the linewidth and the second moment increase at low temperatures (1). From the above it becomes clear that this effect is a general one, being a reflection in NMR of quite a common phenomenon—antiplasticization.

Thus, even an approximate theoretical analysis of the effect of plasticizer content on the NMR linewidth δH allows one to come to certain conclusions concerning the manifestation of antiplasticization in nuclear magnetic resonance. These conclusions can be summarized as follows.

1. The increase in δH with increasing concentration ξ (antiplasticization) is possible only when the polymer is compatible with the plasticizer.

2. This effect can be observed only in the glassy state (i.e., at low temperatures).

3. For the same polymer-plasticizer system δH increases with increasing ξ at low temperatures (at $T < T_g$) and diminish at high temperatures ($T > T_g$).

4. Both these dependences of δH on ξ lend themselves to a theoretical description.

6.2.4. Effect of Structure and Composition on the Second Moment and the Spin-Lattice Relaxation Time

In order to find out how the polymer structure affects the second moment and the spin-lattice relaxation time, we shall make use of Eq. (6.9). Introducing the notation $Q = T_1 \Delta H_2^2$, we can write Eq. (6.9) in the following form:

$$\frac{1}{Q} = \frac{2}{3} (f_1 + f_2) \quad (6.19)$$

where f_1 and f_2 are the first and second integrals on the right-hand side of Eq. (6.9). It is obvious that f_1 and f_2 depend on the correlation-time spectrum $I(\tau_c)$, τ_c , and ω .

Let us consider, for example, the effect of the plasticizer concentration on the ΔH_2^2 and T_1 of polymers. For this purpose, using the arguments given above and substituting the expression for $I(\tau_c)$ of the type (6.17) into f_1 and f_2 , we reduce Eqs. (6.9) and (6.19) to the following form:

$$\begin{aligned} \frac{1}{Q} = \frac{1}{T_1 \Delta H_2^2} = \frac{2}{3} \left\{ \xi \left[\int_0^\infty \frac{I_1(\tau_c) \tau_c d\tau_c}{1 + \omega^2 \tau_c^2} + 4 \int_0^\infty \frac{I_1(\tau_c) \tau_c d\tau_c}{1 + 4\omega^2 \tau_c^2} \right] + \right. \\ \left. + (1 - \xi) \left[\int_0^\infty \frac{I_2(\tau_c) \tau_c d\tau_c}{1 + \omega^2 \tau_c^2} + 4 \int_0^\infty \frac{I_2(\tau_c) \tau_c d\tau_c}{1 + 4\omega^2 \tau_c^2} \right] \right\} \quad (6.20) \end{aligned}$$

It is obvious that if the predominant contribution to the right-hand side of Eq. (6.20) is made by the sum of integrals, having the factor $(1 - \xi)$, the parameter Q will increase with increasing plasticizer concentration. This case occurs at low temperatures (below T_g). Under these conditions (with the phenomenon of antiplasticization) the product of the longitudinal spin-lattice relaxation time T_1 by ΔH_2^2 increases with increasing plasticizer concentration. Since the intensification of intermolecular interaction and the suppression of molecular motion are typical of this case, it is evident that the increase in Q is associated with the increase of the spin-lattice relaxation time as well as of the second moment.

At high temperatures (above T_g) the predominant contribution to the value of $1/Q$ is made by the integrals which have the factor ξ

before them. As the plasticizer concentration increases the value of the parameter $Q = T_1 \Delta H_2^2$ will diminish, which is ascribed to the decrease of both cofactors (T_1 and ΔH_2^2).

The effect of the degree of crystallinity and the network density on T_1 and ΔH_2^2 can be considered in an analogous way.

6.3. Investigation of Molecular Motion by NMR

The results of numerous experimental investigations show that as the temperature falls the various modes of molecular motion in polymers become gradually frozen. This increases the second moment, which at very low temperatures tends to theoretical values calculated for the rigid lattice. As a rule, the freezing of molecular motion in polymers with decreasing temperature may be regarded as a thermal-activation process resulting from the fact that the energy of thermal motion of a particular kinetic unit diminishes, and when it becomes less than the height of the potential barrier that hinders its motion the given type of molecular motion becomes impossible. As a result, the second moment ΔH_2^2 and the spin-lattice relaxation time T_1 increase.

Usually, in order to investigate molecular motion in polymers by NMR spectroscopy, use is made of the temperature dependence of the second moment ΔH_2^2 . If the polymer cooled down to a very low temperature is gradually heated, the value of ΔH_2^2 must decrease as each type of molecular motion is being unfrozen. Naturally, the most noticeable decrease in the second moment must be observed when all segmental motions become unfrozen, i.e., upon transition from the glassy to the rubbery state. Determination of the temperature region in which there occurs a considerable decrease in the value of ΔH_2^2 is one of the methods of identification of the glassy region. This refers largely to amorphous polymers.

Let us consider the variation of the second moment caused by molecular mobility in one of the simplest (as to chemical structure) polymers—polyisobutylene. The temperature dependence of the second moment of NMR in this polymer (22) is shown in Fig. 6.5. The second moment at room temperature in polyisobutylene is 0.2 G^2 . As the temperature falls the second moment increases and attains the value 33.6 G^2 at 77 K . Further decrease in temperature leads to a decrease in ΔH_2^2 , while in the temperature range $5\text{--}30 \text{ K}$ the second moment remains constant at 26 G^2 . Calculations based on the van Vleck theory give a value of $\Delta H_2^2 = 40.3 \text{ G}^2$ for the rigid lattice. The rotation of one methyl group lowers the second moment down to 25.9 G^2 , and the rotation of both CH_3 groups reduces it to 12.5 G^2 .

In polyisobutylene above 200 K one observes a sharp decrease in ΔH_2^2 , which at $T = 293 \text{ K}$ assumes a very low value which corre-

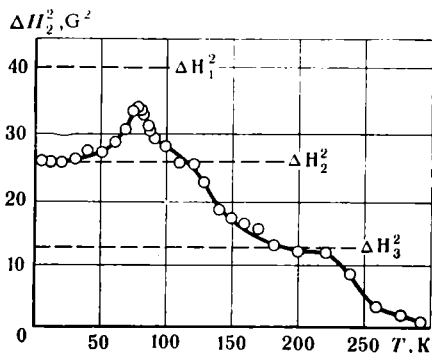


Fig. 6.5. Temperature dependence of the second moment ΔH_2^2 of polyisobutylene:

$(\Delta H_2^2)_1$ is a theoretical value for the rigid lattice; $(\Delta H_2^2)_2$ is a theoretical value corresponding to the tunnelling of methyl groups; $(\Delta H_2^2)_3$ is a theoretical value taking account of the rotation of two CH_3 groups.

sponds to the rubbery state. The region of rapid change in the second moment corresponds to the glass-transition region of this polymer. The second moment at 200 K is 12.6 G^2 , which value can be attributed to the rotation of both methyl groups and is in good agreement with the theoretically calculated value (12.5 G^2). Further increase in the second moment with decreasing temperature is caused by the freezing of the rotational motion of the CH_3 groups. At 110 K a slight kink on the $\Delta H_2^2 = f(T)$ graph appears—the second moment at this temperature is equal to 26 G^2 and coincides with the theoretically predicted value (25.9 G^2), which corresponds to the rotation of only one CH_3 group in the repeating unit of the polymer. With a further drop in temperature the second moment reaches its maximum value, 33.6 G^2 , at 77 K. This value differs greatly (by 6.7 G^2) from the second moment corresponding to the rigid lattice (40.3 G^2). Such a large difference between these values signifies that at 77 K the mobility of the CH_3 groups is still considerable.

The fall of the second moment as the temperature drops below 77 K is an indication that the observed effect is not thermal activation and, hence, cannot be accounted for on the basis of the classical conceptions of the rotation of methyl groups. Classical physics cannot account for the fact that the second moment in polyisobutylene down to 5 K remains to be much lower than the value of $\Delta H_2^2 = 40.3 G^2$ calculated theoretically for the rigid lattice. This is an indication that molecular motion in polyisobutylene is retained even at 5 K. It is well known (1, 8-10) that the lowest-temperature type of molecular motion in such a polymer must be associated with the rotation of CH_3 groups. It is not difficult, however, to show that the height of the barrier that hinders the rotation of methyl groups is not lower than 8.4 kJ and at $T < 40$ K the classical rotation of methyl groups cannot lead to a change in ΔH_2^2 since the energy of methyl groups under these conditions is found to be much lower than the potential barrier height. In this connection, a supposition has been advanced that the re-orientation of methyl groups with respect

to the C_3 axis near 0 K has a quantum nature and is caused by quantum-mechanical tunnelling transitions.

From the standpoint of the concepts of classical physics, the potential barrier of height U is a "non-transparent" partition for all particles with energy $E < U$. A quantum-mechanical treatment of the motion of microparticles in microscopical fields shows that in a number of cases particles with energy $E < U$ can tunnel through the potential barrier.

Powles and Gutowsky (23) have shown that at low temperatures some of the methyl groups experience torsional vibrations (re-orientational motion) about the C_3 axis as a result of tunnelling through the barrier (at $E < U$) that hinders their classical rotation. Such tunnelling of CH_3 groups leads to a decrease in ΔH_2^2 for polymers containing methyl groups at $T \rightarrow 0$ K as compared with the value of the second moment calculated for the rigid lattice. The theory of quantum-mechanical tunnelling of CH_3 groups has been expounded by Stejskal and Gutowsky (24), who used it for calculation of the tunnelling frequency and the spin-lattice relaxation time T_1 . This theory rests on the assumption that the methyl groups are separated from one another and are linked to the immobile chain matrix. It is presumed further that the potential of the retarded (frozen) rotation of the methyl group does not depend on time and can be given by

$$U = \frac{1}{2} U_0 (1 + \cos 3\Phi) \quad (6.21)$$

where U_0 is the height of the potential barrier; Φ is the angle of rotation of the CH_3 group.

Substituting the potential function defined by expression (6.21), into the Schrödinger equation, we obtain:

$$\frac{\hbar^2}{2I} \cdot \frac{\partial^2 \psi(\Phi)}{\partial \Phi^2} + \left\{ E - \frac{U_0}{2} (1 + \cos 3\Phi) \right\} \psi(\Phi) = 0 \quad (6.22)$$

where $\psi(\Phi)$ is the wave function defining the position of the methyl group; E is the energy of the methyl group; I is the moment of inertia of the methyl group relative to the axis of symmetry.

Solving Eq. (6.22) gives a set of the eigenvalues of energy E_i which correspond to the levels of torsional vibrations of a methyl group having a potential with a three-fold symmetry. As a result of the splitting of energy levels, the methyl group can be simultaneously in two neighbouring potential wells. A consequence of this is that part of the methyl groups can move with a non-zero probability from one potential well to an identical energy level in another potential well. This makes possible the re-orientational motion of methyl groups about the C_3 axis by tunnelling through the potential barrier. The tunnelling frequency depends on the height of the potential barrier U_0 and the energy E_i of the methyl group. The split-

ting Δv is a measure of the velocity with which the methyl group tunnels through the potential barrier. If the energy of the methyl group appears to be greater than the potential barrier U_0 with increasing temperature, the quantum-mechanical tunnelling changes to classical rotation.

The tunnelling frequency of the methyl group at temperature T can be given by

$$v_T = \frac{1}{Q} \sum_i \Delta v_i \exp \left(-\frac{E_i}{RT} \right) = \sum_i a_i \Delta v_i \quad (6.23)$$

where Q is the partition function for torsional vibrations; a_i is the probability that the methyl group is in the i th vibrational state.

Obviously, v_T is the average tunnelling frequency for the entire set of energy levels existing at a given temperature. Stejskal and Gutowsky calculated the dependence of v_T on temperature for potential barriers of various heights ranging from 9.89 and 33.35 kJ. It is remarkable that below 70 K the average tunnelling frequency does not depend on temperature. This means that the re-orientation of methyl groups occurring through this mechanism is possible down to 0 K. One would think that the dependence $\Delta H_2^2 = f(T)$ in polyisobutylene at low temperatures can be explained quantum-mechanically. However, the simple quantum-mechanical tunnelling model described in the literature (23-24) does not allow one to account for the decrease in the second moment at $T \rightarrow 0$ K. This effect cannot be explained either with the aid of the more complicated Allen model (25). Allen calculated ΔH_2^2 on the basis of a more accurate energy-level diagram for the methyl group. This is largely associated with the fact that these models deal with the motion of the methyl group in an isolated molecule.

Clough (26) attempted to calculate the motion of the methyl group in a molecular crystal. He assumed that the motion of the methyl group alters the lattice state. Consideration of this phenomenon leads to the appearance, in expression (6.24) for the hindering potential, of an additional term due to the reverse action of the effect of a change in the lattice state on the methyl group. Using this potential, Clough calculated the energy-level diagram for the methyl group. His calculations were based on the assumption that the splitting of the energy level corresponding to the joint state of the methyl group and the lattice is small as compared with kT .

The Clough theory allows one to account for the existence of a maximum in the temperature dependence of the second moment in polyisobutylene, and other polymers. At the lowest temperatures the value of the second moment in polyisobutylene (26 G²), which is low as compared with the ΔH_2^2 value for the rigid lattice, is due to the re-orientation of the methyl groups resulting from quantum-

mechanical tunnelling. As the temperature rises the intensity of lattice vibrations increases. These lattice vibrations cause a sort of tunnelling frequency modulation, which leads to a decrease in the tunnelling motion of methyl groups as the temperature rises. This effect is especially pronounced when the extent of tunnelling frequency modulation is sufficiently great and the probability of classical rotation is still low. Thus, one can expect that at sufficiently low temperatures the second moment will increase with increasing temperature, tending towards the value typical of the rigid lattice. Further rise of temperature leads to an increase in the energy of thermal motion (thermal activation) of methyl groups and to the unfreezing of classical rotation and, hence, to a decrease in ΔH_2^2 .

Thus, by taking account of the lattice vibrations one is able to explain the increase in ΔH_2^2 with rise of temperature at low temperatures. From the conceptions expounded above one can expect that the increase in ΔH_2^2 with rise of temperature will depend on steric hindrances that impede the motion of methyl groups.

References

1. Slonim, I. Ya. and A. N. Lyubimov, *NMR of Polymers*, Plenum Press, New York, 1970.
2. Skripov, F. I., *A Course of Lectures in Radiospectroscopy*, Izdat. LGU (Leningrad University Press), Leningrad, 1964 (in Russian).
3. Roberts, J. D., *Nuclear Magnetic Resonance*, McGraw-Hill Book Co., New York, 1959.
4. Lösche, A., *Kerninduktion*, Deutsche Verlag der Wissenschaften, Berlin, 1957.
5. Slichter, Ch. P., *Principles of Magnetic Resonance with Examples from Solid State Physics*, Harper Row, New York, 1963.
6. Slichter, W. P., *Macromol. Chem.*, **34**, 67 (1959).
7. Aleksandrov, N. M. and F. I. Skripov, *Uspekhi Fiz. Nauk*, **75**, 4, 585 (1961).
8. Slichter, W. P., *Erg. exact. Naturwiss* (1958).
9. Slonim, I. Ya., *Uspekhi Khim.*, **31**, 5, 609 (1962).
10. Slichter, W. P., in: *Transitions and Relaxations in Polymers*, Interscience Publishers, New York, 1966.
11. Van Vleck, J. H., *Phys. Rev.*, **74**, 9, 1168 (1948).
12. Bloembergen, N., E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 7, 679 (1948).
13. Mijake, A., *J. Polymer Sci.*, **28**, 117, 476 (1958).
14. Grigoriev, V. P. and A. I. Maklakov, *Vysokomol. Soedin.*, **A**, **15**, 11, 2576 (1973).
15. Grigoriev, V. P., V. M. Lantsov, A. I. Maklakov, and A. A. Lantsova, *Fizika Tverdogo Tela*, **9**, 12, 3635 (1967).
16. Chujo, R., *J. Phys. Soc. Japan*, **18**, 1, 124 (1963).
17. McCall, D. W. and W. P. Slichter, *J. Polymer Sci.*, **26**, 113, 171 (1957).
18. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers, Moscow, 1975.
19. Matochkin, V. S. et al., *Doklady Akad. Nauk SSSR*, **204**, 6, 1359 (1972).

20. Fujiwara, S., A. Amamia, and K. Shinohara, *J. Chem. Phys.*, **26**, 5, 1343 (1957).
21. Gupta, R. P., *J. Phys. Chem.*, **65**, 7, 1128 (1961).
22. Kosfeld, R. and U. Mylius, *Koll.-Z. u. Z. Polymere*, **250**, 11-12, 1088 (1972).
23. Powles, J. G. and H. S. Gutowsky, *J. Chem. Phys.*, **23**, 9, 1692 (1955).
24. Stejskal, E. O., and H. S. Gutowsky, *J. Chem. Phys.*, **28**, 3, 388 (1958).
25. Allen, P. S., *J. Chem. Phys.*, **48**, 7, 3031 (1968).
26. Clough, S., *J. Phys. C. Solid State Phys.*, **4**, 14, 2180 (1971).

Viscoelastic Properties of Polymers

7.1. Basic Information on Viscoelastic Behaviour

One of the remarkable features of polymers lies in their sharply pronounced viscoelastic properties. Viscoelastic behaviour is responsible for a unique combination of the main physico-mechanical properties of polymers.

We know that for most solids, especially in the case of very small strains, Hooke's law in its simplest form is satisfied:

$$\sigma = ES \quad (7.1)$$

where σ is the stress; S is the strain; E is the elastic modulus. The behaviour of low-viscosity liquids usually obey Newton's law well:

$$\sigma_{xy} = \eta \frac{\partial v_x}{\partial y} \quad (7.2)$$

where σ_{xy} is the shear stress; $\partial v_x / \partial y$ is the velocity gradient of the liquid; η is the viscosity coefficient.

As a matter of fact, there are no ideal Newtonian liquids completely deprived of elasticity, just as there are no ideal elastic bodies obeying Hooke's law under any deformation conditions. All real bodies possess, in some measure, both elastic and viscous properties. The viscoelastic behaviour of many materials, however, is not marked, for which reason they are usually classified as either elastic or viscous.

Polymeric materials exhibit, as a rule, the properties of both elastic bodies and some of the properties of liquids. This leads to a specific relationship between stress and strain.

7.1.1. Stress-Strain Relations

In the case of viscoelastic bodies, the relation between the stress σ , which varies according to a sinusoidal law, and the strain S may be written in the form:

$$\sigma = E^* S \quad (7.3)$$

where E^* is the complex elastic modulus defined by

$$E^* = E' + iE'' \quad (7.4)$$

The real part of the elastic complex modulus, $\text{Re } E^* = E'$, is known as the dynamic or storage modulus, and the imaginary part, $\text{Im } E^* = E''$, is called the loss modulus.

Expression (7.3) is of prime importance for the description of the behaviour of polymeric materials under a periodically varying stress. Suppose that a body is subjected to a sinusoidally varying stress $\sigma = \sigma_0 \cos \omega t$, where t is the time, $\omega = 2\pi f$ is the circular frequency (f is the number of vibrations per second), and σ_0 is the amplitude of the stress. In this case, if the body displays linear viscoelastic behaviour, the strain will also vary sinusoidally but will be out of phase with the stress, $S = S_0 \cos(\omega t - \delta)$, where S_0 is the amplitude of the strain and δ is the phase difference (or the phase angle) between stress and strain.

At any time

$$E^* = \sigma/S \quad (7.5)$$

The sinusoidally varying stress, which is not in phase with the strain, can be resolved into two components, one of which will be in phase with the strain and the second will be $\pi/2$ out of phase with the strain; this clarifies the meaning of the quantities E' and E'' .

7.1.2. The Dynamic Elastic Modulus

The storage modulus is usually taken to mean the stress at which the relative deformation of a material is equal to unity. In the case of viscoelastic bodies this definition must be generalized.

The storage modulus E' is the real part of the complex modulus and is equal to the ratio of the stress component in phase with the strain to the amount of this strain. The storage modulus is a measure of the energy gained and lost by the volume element of a body per cycle.

It will be shown at a later time that at absolute vibration amplitude E' increases or remains constant with increasing frequency.

7.1.3. The Loss Modulus

The loss modulus E'' is the ratio of the stress component, which is $\pi/2$ out of phase with the strain, to the amount of the strain. The loss modulus E'' is a measure of that part of the energy of elastic vibrations which is converted into heat per cycle of vibrations. The larger the phase difference between stress and strain, the higher the value of E'' . In those cases where the phase difference between stress and strain becomes largest, E'' passes through a maximum. Thus, E'' characterizes the dissipation of vibrational energy in a viscoelastic body.

The absolute value of the complex modulus is equal to $|E^*| = \sqrt{E'^2 + E''^2}$; on the other hand, the ratio of the amplitudes of the stress and strain is $\sigma_0/s_0 = \sqrt{E'^2 + E''^2}$. The phase difference between stress and strain is usually specified by the loss tangent $\tan \delta = E''/E'$, which is also called the loss factor.

Sometimes, use is made of the concept of the complex compliance:

$$J^* = \frac{1}{E^*} = J' - iJ'' \quad (7.6)$$

The quantity J' is called the dynamic compliance and J'' is the loss compliance. Despite the simple relationship between J^* and E^* , the components of the complex compliance and E^* are interrelated in a different manner:

$$J^* = \frac{\frac{1}{E'} - i \frac{1}{E'} \tan \delta}{1 + \tan^2 \delta} \quad (7.7)$$

Comparing expressions (7.6) and (7.7), we obtain:

$$J' = \frac{1/E'}{1 + \tan^2 \delta} = \frac{1}{E' (1 + \tan^2 \delta)} \quad (7.8)$$

$$J'' = \frac{1/E''}{1 + (\tan^2 \delta)^{-1}} = \frac{\tan \delta}{E' (1 + \tan^2 \delta)} \quad (7.9)$$

So far the quantity E^* has been taken to imply an arbitrary modulus of elasticity and what we have said about E^* , J^* and their components is valid for any type of strain and for any elastic modulus in the case of an isotropic viscoelastic body.

The viscoelastic behaviour of an isotropic body can be fully described with the aid of two independent complex moduli of elasticity, say, by Young's modulus E^* and the complex shear modulus G^* . The other viscoelastic functions can be calculated if E^* and G^* are known. The complex Poisson's ratio can be defined by the relation

$$\nu^* = \nu' - i\nu'' = \frac{E^*}{2G^*} - 1 \quad (7.10)$$

The complex bulk modulus is given by

$$K^* = K' + iK'' = \frac{E^*}{3} \frac{1}{1 - 2\nu^*} \quad (7.11)$$

One of the simplest and most reliable methods of determination of the components of the elastic moduli is the calculation from experimental data on the measurement of the sound velocity and the sound absorption coefficient.

7.1.4. Velocity and Absorption of Elastic Waves

Elastic waves are appreciably damped in polymers. In this process, there is observed a strong frequency dependence (dispersion) of the sound velocity. The expression for the displacement of particles in the case of a longitudinal wave which propagates in the direction of the x axis may be represented in the form

$$U = U_0 e^{i\omega t - Kx}$$

where U_0 is the displacement amplitude; t is the time; K is the complex wavenumber; $K = \alpha + i\beta = \alpha + i(\omega/c)$, where α is the acoustic absorption coefficient, $c = \lambda f$ is the velocity of elastic waves, and λ is the wavelength.

Several types of wave can propagate in solids. In an infinite medium, i.e., in cases where the wavelength λ is considerably less than the lateral dimensions of the body d ($\lambda \ll d$), the velocity of a pure longitudinal wave is expressed by the following formula provided that the damping is sufficiently low:

$$c_L = \sqrt{\frac{K'_s + 4/3 G'}{\rho}} \quad (7.12)$$

where K'_s is the dynamic bulk (or volume) modulus of elasticity; G' is the dynamic shear modulus.

The expression for the velocity of a longitudinal wave in an infinite medium can be written in a different form:

$$c_L = \sqrt{\frac{E'}{\rho} \frac{(1-\nu')}{(1+\nu')(1-2\nu')}} \quad (7.13)$$

where E' is Young's modulus; ν' is Poisson's ratio; ρ is the density of the medium in which the wave is propagating.

The velocity of longitudinal waves is sometimes written in the following form:

$$c_L = \sqrt{L'/\rho} \quad (7.14)$$

where L' is the longitudinal dynamic elastic modulus or the "effective modulus of a longitudinal wave".

It is obvious that

$$L^* = L' + iL'' = K_s^* + \frac{4}{3} G^* \quad (7.15)$$

In the case of waves propagating in thin rods (polymeric fibres, thin film strips), when $\lambda \gg d$ (where d characterizes the lateral dimensions of the body), the velocity of longitudinal waves is expressed by the formula

$$c_L = \sqrt{E'/\rho} \quad (7.16)$$

The velocity of shear (or transverse) waves, in which the vibrations occur in a direction perpendicular to the direction of wave propagation, may be represented in the form

$$c_T = \sqrt{G'/\rho} \quad (7.17)$$

where G' is the dynamic shear modulus. It should be noted that formulas (7.12) through (7.17) are approximate and hold only in those cases where $\alpha\lambda/2\pi \ll 1$, i.e., when the damping per wavelength is small. In a general case, the relationship between the velocity c , the acoustic absorption coefficient and the components of the complex elastic modulus $M^* = M' + iM''$ is expressed by the following formulas:

$$M' = \frac{\rho c^2 \left[1 - \left(\frac{\alpha\lambda}{2\pi} \right)^2 \right]}{\left[1 + \left(\frac{\alpha\lambda}{2\pi} \right)^2 \right]} \quad (7.18)$$

$$M'' = \frac{2\rho c^2 \frac{\alpha\lambda}{2\pi}}{\left[1 + \left(\frac{\alpha\lambda}{2\pi} \right)^2 \right]^2} \quad (7.19)$$

For the corresponding types of wave (those mentioned above), the components of M^* should be replaced by the components of the complex moduli L^* , E^* and G^* , and the velocities and absorption coefficients of the corresponding waves (c_L , c , and c_T) should be used.

The measurement of the sound velocity is one of the most convenient methods for the determination of Poisson's ratio. The complex Poisson's ratio is given by the relation

$$\nu^* = \nu' - i\nu'' = \frac{L^* - 2G^*}{2(L^* - G^*)} \quad (7.20)$$

One of the most important methods is the determination of the real part ν' , which can be found from the following approximate formula:

$$\nu' = \frac{1}{2} \frac{L' - 2G'}{L' - G'} \quad (7.21)$$

It is known that the amplitude of vibration of particles in a propagating wave decays with distance according to an exponential law: $U = U_0 e^{-\alpha x}$. If we know the values of U_1 and U_2 at points with the coordinates x_1 and x_2 for a plane sound wave, the attenuation constant is found from the formula:

$$\alpha = \frac{1}{x_2 - x_1} \ln \frac{U_1}{U_2} \quad (7.22)$$

The attenuation constant has the dimensions of cm^{-1} ; sometimes it is expressed in Np/cm. Since 1 neper is the ratio of two quantities

which have the same dimensions and differ by e times ($e = 2.71$), it follows that $1/\alpha$ indicates the length of the sound path on which the amplitude decays by e times. Sometimes, the damping factor is measured in decibels per centimetre (dB/cm); 1 Np/cm is equal to 8.686 dB/cm.

7.2. Phenomenological Theory of Viscoelastic Properties

7.2.1. Basic Equations

The main parameters that characterize the viscoelastic behaviour of polymers include the dynamic elastic moduli, the loss moduli, the loss factor $\tan \delta$ and also the sound velocity and the acoustic absorption coefficient.

The principal objective of the theory that describes the viscoelastic behaviour of polymers is the establishment of the relationship between these parameters and the frequency and temperature, and also of their dependence on the chemical and physical structure. There are several methods of describing the viscoelastic properties of polymers (1). Some of them are based on the use of mechanical or electrical models, i.e., the methods of electromechanical analogies, and the others make use of the Boltzmann-Volterra after-effect equations (2, 3).

One of the possible methods of describing the viscoelastic behaviour of polymers rests on the theory of elasticity and some of the concepts of the thermodynamics of irreversible processes (4).

In this connection, let us consider the propagation of a plane sound wave in a viscoelastic heat-conducting medium. Usually, in the solution of problems of this kind, heat conduction is disregarded. But when one is dealing with the propagation of ultrasonic waves in polymers at low temperatures, thermal conductivity becomes an important factor.

We choose, as the basic equations, the laws of conservation of mass, momentum, and energy, which can be formulated in the following manner for a one-dimensional case:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \rho \frac{\partial v_x}{\partial x} &= 0 \\ \rho \frac{\partial^2 U}{\partial t^2} - \frac{\partial \sigma_{xx}}{\partial x} &= 0 \\ \rho c_v \frac{\partial T}{\partial t} - \frac{T\beta K_T}{\rho} \frac{\partial \rho}{\partial t} + \frac{\partial q_x}{\partial x} &= 0 \end{aligned} \quad (7.23)$$

where U is the displacement of the points within the body upon deformation; $v_x = \dot{U}_x$ is the velocity of the particles of the medium;

σ_{xx} is the diagonal component of the stress tensor; T is the temperature; c_v is the specific heat at constant volume; $\beta = (1/V) (\partial V / \partial T)_p$ is the thermal cubic expansion coefficient; ρ is the density of the medium; V is the specific volume; $K_T = -V (\partial p / \partial V)_T$ is the isothermal compressibility; q_x is the component of the heat flux density vector ($q = -\kappa \nabla T$, where κ is the thermal conductivity coefficient).

In order to integrate the system of equations (7.23) one must find expressions for the stress tensor σ_{ik} and the heat flux density vector \bar{q} which would be valid for a viscoelastic medium.

The stress tensor for an isotropic viscoelastic body can be written in the form

$$\bar{\sigma}_{ik} = \sigma_{ik} + \sigma'_{ik} \quad (7.24)$$

where σ_{ik} is the stress tensor for an elastic solid; σ'_{ik} is the "dissipation" stress tensor.

We know (5) that in an elastically deformed body

$$\sigma_{ik} = \left(\frac{\partial F}{\partial U_{ik}} \right)_T \quad (7.25)$$

where F is the Helmholtz free energy of the deformed body; U_{ik} is the strain tensor.

Since the "dissipation" stress tensor has the same form as the viscous stress tensor for liquids, it follows that

$$\begin{aligned} \bar{\sigma}_{ik} = & -K_T \beta (T - T_0) \delta_{ik} + 2G \left(U_{ik} - \frac{1}{3} \delta_{ik} U_{ll} \right) + \\ & + K_T U_{ll} \delta_{ik} + 2\eta \left(\dot{U}_{ik} - \frac{1}{3} \delta_{ik} \dot{U}_{ll} \right) + \eta' \dot{U}_{ll} \delta_{ik} \end{aligned} \quad (7.26)$$

where $\eta = G\tau_1$ is the shear viscosity coefficient; G is the shear modulus; τ_1 is the relaxation time; $\eta' = K_T \tau_2$ (τ_2 is the corresponding relaxation time).

Expression (7.26) can be written in the form

$$\bar{\sigma} = -K_T \beta (T - T_0) + S + Z + S' + Z' \quad (7.27)$$

One might expect that, as a result of the rapidly changing gradients that arise during the propagation of a sound wave, the values of S' , Z' and q would be different from the values of S'_0 , Z'_0 and q_0 which correspond to the steady-state gradients. Assuming that the deviations of S' , Z' and q from S'_0 , Z'_0 and q_0 are not large, we can

write the following response equation (4):

$$\frac{\partial S'}{\partial t} = -\frac{1}{\tau_1} (S' - S'_0) \quad (7.28)$$

$$\frac{\partial Z'}{\partial t} = -\frac{1}{\tau_2} (Z' - Z'_0) \quad (7.29)$$

$$\frac{\partial q}{\partial t} = -\frac{1}{\tau_3} (q - q_0) \quad (7.30)$$

Having extended expressions (7.28), (7.29) and (7.30) to the case of an inhomogeneous material with an arbitrary number of relaxation processes, one can show that

$$\sigma_{xx} = -K_T \beta (T - T_0) + \hat{L} \frac{\partial U}{\partial x} \quad (7.31)$$

Here the differential operator \hat{L} is given by

$$\hat{L} = \hat{K}_T + \frac{4}{3} \hat{G} \quad (7.32)$$

where

$$\hat{K}_T = K_T + \sum_{j=1}^n \frac{K_{Tj} \tau_{2j} \frac{\partial}{\partial t}}{1 + \tau_{2j} \frac{\partial}{\partial t}} \quad (7.33)$$

$$\hat{G} = G_0 + \sum_{j=1}^n \frac{G_{0j} \tau_{1j} \frac{\partial}{\partial t}}{1 + \tau_{2j} \frac{\partial}{\partial t}} \quad (7.34)$$

In the case of periodic harmonic processes the differential operators (7.33) and (7.34) become:

$$\hat{K}_T = K_T + \sum_{j=1}^n \frac{K_{Tj} i \omega \tau_{2j}}{1 + i \omega \tau_{2j}} \quad (7.33a)$$

$$\hat{G} = G_0 + \sum_{j=1}^n \frac{G_{0j} i \omega \tau_{1j}}{1 + i \omega \tau_{1j}} \quad (7.34a)$$

In an analogous way, for the case of periodic harmonic processes we obtain:

$$q = - \left(\sum_{j=1}^n \kappa_{0j} / 1 + i \omega \tau_{3j} \right) \nabla T \quad (7.35)$$

where

$$\kappa_j = \frac{\kappa_{0j}}{1 + i \omega \tau_{3j}}$$

is the effective ("dynamic") thermal conductivity coefficient which is characterized by the relaxation time τ_{3j} ; κ_{0j} is the static thermal conductivity coefficient corresponding to low frequencies ω (at $\omega \rightarrow 0$).

Substituting expressions (7.31), and (7.35) into Eq. (7.23) and solving this system of equations, we can obtain (4) the following expressions for the velocity of propagation of a longitudinal sound wave in a viscoelastic medium and the acoustic absorption coefficient:

$$c^2 = c_0^2 \left[1 + \frac{1}{\rho c_0^2} \left(\frac{4}{3} \sum_{j=1}^n \frac{G_{0j} \omega^2 \tau_{1j}^2}{1 + \omega^2 \tau_{1j}^2} + \sum_{j=1}^n \frac{K_{Tj} \omega^2 \tau_{2j}^2}{1 + \omega^2 \tau_{2j}^2} + \sum_{j=1}^n \frac{\omega^2 \tau_{3j}^2 \chi_{0j} \rho D}{1 + \omega^2 \tau_{3j}^2} \right) \right] \quad (7.36)$$

$$\frac{\alpha \lambda}{2\pi} = \frac{1}{2\rho c^2} \left\{ \frac{4}{3} \sum_{j=1}^n \frac{G_{0j} \omega \tau_{1j}}{1 + \omega^2 \tau_{1j}^2} + \sum_{j=1}^n \frac{K_{Tj} \omega \tau_{2j}}{1 + \omega^2 \tau_{2j}^2} + \rho D \sum_{j=1}^n \frac{\omega \tau_{3j} \chi_{0j}}{1 + \omega^2 \tau_{3j}^2} \right\} \quad (7.37)$$

Here

$$D = \frac{c_0^2 - b_0^2}{c_0^2}$$

where

$$b_0^2 = \left(K_T + \frac{4}{3} G_0 \right) / \rho \quad (7.38)$$

$$c_0^2 = \left(K_s + \frac{4}{3} G_0 \right) / \rho \quad (7.39)$$

$$\chi_0 = \kappa_0 / (\rho c_0) \quad (7.40)$$

The quantity K_s is the adiabatic compressibility; χ is the thermal conductivity coefficient.

Passing over to a continuous spectrum, we obtain

$$\rho c^2 = \rho c_0^2 + \int_0^\infty \frac{H(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (7.41)$$

$$\frac{\alpha \lambda}{2\pi} = \frac{1}{2\rho c^2} \int_0^\infty \frac{H(\tau) \omega \tau}{1 + \omega^2 \tau^2} d\tau \quad (7.42)$$

where

$$H(\tau) = \frac{4}{3} H_1(\tau) + H_2(\tau) + \rho D H_3(\tau)$$

and each of the functions $H_1(\tau)$, $H_2(\tau)$ and $H_3(\tau)$ represents the relaxation time spectrum density.

Thus, the use of the equations corresponding to the basic laws of conservation enables one to obtain expressions for the acoustic absorption coefficient and the velocity of propagation of sound waves in viscoelastic heat-conducting materials (most polymers are precisely such materials).

It can be shown (4) that the use of response equations for the elements of the strain tensor leads to the following expression for the compliance operator:

$$\hat{J} = \frac{1}{G_\infty} + \sum_{j=1}^n \frac{1}{G_{0j}} \frac{1}{1 + i\omega\tau_j} \quad (7.43)$$

For the sound velocity we obtain accordingly:

$$\frac{1}{c^2} = \frac{1}{c_q^2} + \rho \int_0^\infty \frac{L(\tau) d\tau}{1 + \omega^2\tau^2} \quad (7.43a)$$

where $L(\tau)$ is the density of the retardation time spectrum, and c_q is the maximum velocity sound (at $\omega\tau \rightarrow \infty$), which is independent of the frequency.

The formulas given above describe satisfactorily (at least, qualitatively) the dynamic viscoelastic properties of polymers.

One of the methods of describing the viscoelastic behaviour of real bodies is the use of mechanical models. The most frequently used models are the Maxwell model, the Kelvin-Voigt model and the rheological model of the standard linear solid. Let us consider these models and show that they can be obtained as consequences of the phenomenological theory expounded above.

7.2.1.1. The Maxwell Model

The simplest mechanical model called the Maxwell model consists of a spring and a viscous element (a dashpot, which is a piston moving in a viscous liquid) in series (Fig. 7.1). This model is sometimes employed for describing stress relaxation experiments. If in expression (7.34a) for the differential operator of the modulus we put the equilibrium modulus $G_0 = 0$ with all the τ_j being equal to zero, except τ , Eq. (7.34a) will become:

$$\hat{G} = \frac{G_1\tau \frac{\partial}{\partial t}}{1 + \tau \frac{\partial}{\partial t}} \quad (7.44)$$

It is evident that relation (7.44) completely coincides with the differential operator of the modulus for a single Maxwell element. The



Fig. 7.1. The Maxwell model.

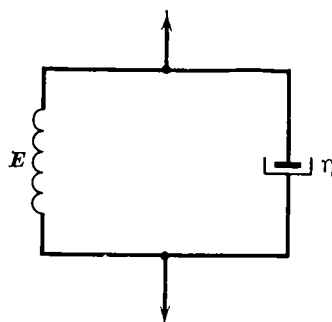


Fig. 7.2. The Kelvin-Voigt model.

complex shear modulus for the case of periodic processes has the form

$$G^* = G' + iG'' = \frac{i\omega\tau G_1}{1 + i\omega\tau} \quad (7.45)$$

From this equation we arrive at the following expressions:

$$G' = \frac{G_1 \omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (7.46)$$

$$G'' = G_1 \frac{\omega\tau}{1 + \omega^2 \tau^2} \quad (7.47)$$

Analysis of formulas (7.46) and (7.47) shows that a single Maxwell body cannot be used for to describe the dynamic viscoelastic properties of polymers. Indeed, from Eq. (7.46) it is seen that in the case of limiting low frequencies (at $\omega\tau \rightarrow 0$) $G' \rightarrow 0$. Thus, in this model the dynamic elastic modulus has no non-zero finite value at $\omega \rightarrow 0$, which contradicts experimental data and points to the incorrectness of the use of this model for describing the dynamic viscoelastic properties of polymers. Besides, for this model $\tan \delta = G''/G' = 1/(\omega\tau)$; this means that $\tan \delta$ has no peak, which does not agree well with experimental findings either.

7.2.1.2. The Kelvin-Voigt Model

In contrast to the Maxwell model, in the Kelvin-Voigt model the spring and dashpot are placed in parallel (Fig. 7.2). This model is often used to describe the creep of viscoelastic materials. The differential operator of the compliance corresponding to this model is not difficult to obtain from formula (7.43) by setting the instantaneous compliance $J_{0j} = 1/G_{\infty} = 0$ and equating all compliances J_{0j} to zero, except one. Then,

$$\hat{J} = \frac{1}{G_0} \frac{1}{1 + \tau \frac{\partial}{\partial t}} \quad (7.48)$$

The complex elastic modulus for the case of periodic processes is obtained from Eq. (7.48) in the form

$$G^* = G' + iG'' = G_0(1 + i\omega\tau) \quad (7.49)$$

whence

$$G' = G_0, \quad G'' = G_0\omega\tau \quad \text{and} \quad \tan \delta = \omega\tau$$

Thus, in the case of the Kelvin-Voigt model the dynamic elastic modulus is independent of the frequency and $\tan \delta$ has no peak in the $\tan \delta$ vs. $\omega\tau$ curve. Both these conditions can hardly be satisfied in such media as polymeric materials, whose viscoelastic properties are very strongly pronounced.

7.2.1.3. The Standard Linear Solid

Suppose that in formula (7.34a) only one of the values of $\tau \neq 0$ and all the other $\tau_j = 0$ but $G_0 \neq 0$. In this case, the differential operator of the modulus has the form

$$\hat{G} = G_0 + \frac{G_1\tau\partial/\partial t}{1 + \tau\partial/\partial t} \quad (7.50)$$

The complex elastic modulus corresponding to these conditions is given by

$$G^* = G' + iG'' = G_0 + \frac{G_1i\omega\tau}{1 + i\omega\tau} \quad (7.51)$$

from which

$$G' = G_0 + \frac{G_1\omega^2\tau^2}{1 + \omega^2\tau^2} \quad (7.52)$$

$$G'' = \frac{G_1\omega\tau}{1 + \omega^2\tau^2} \quad (7.53)$$

Formulas (7.50) through (7.53) are in full agreement with the mechanical model of the standard linear viscoelastic solid (Fig. 7.3). Let us consider the dependence of G' on the parameter $\omega\tau$. At $\omega\tau = 0$ we have $G' = G_0$; at $\omega\tau \rightarrow \infty$, $G' = G_\infty = G_0 + G_1$. Hence, in the case of a material corresponding to the standard linear solid, the dynamic modulus has finite non-zero values both at $\omega \rightarrow 0$ and at $\omega \rightarrow \infty$.

It is not difficult to show that for this model

$$\tan \delta = 2 \tan \delta_m \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} \quad (7.54)$$

where

$$2 \tan \delta_m = \frac{G_\infty - G_0}{\sqrt{G_\infty \cdot G_0}}$$

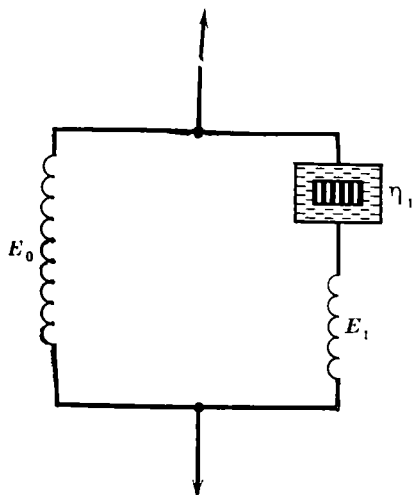


Fig. 7.3. The mechanical model of the standard linear viscoelastic body.

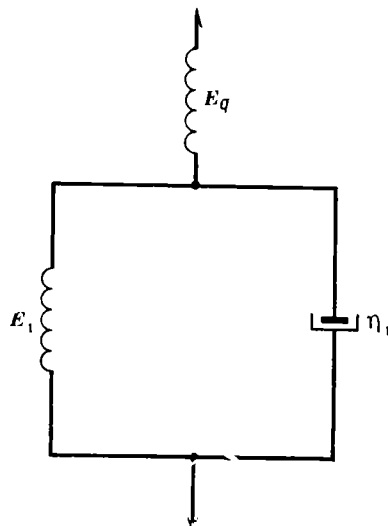


Fig. 7.4. The mechanical model corresponding to relation (7.58).

and the relaxation time τ_1 differs from τ , which is the relaxation time figuring in formulas (7.51) through (7.53):

$$\tau_1 = \sqrt{\frac{G_\infty}{G_0}} \tau$$

It is easy to notice that $\tan \delta$ has a maximum at $\omega \tau_1 = 1$. The quantity ΔG characterizes both the height of the mechanical loss peak and the amount of dispersion (frequency dependence) of the elastic modulus and is called the degree of relaxation:

$$2 \tan \delta_m = (G_\infty - G_0) / \bar{G} = \Delta G \quad (7.55)$$

where

$$\bar{G} = \sqrt{G_\infty \cdot G_0}$$

Sometimes ΔG is called the “defect of the modulus”. It is obvious that $\tan \delta_m = 0.5 \Delta G$.

The degree of relaxation for the various elastic moduli of a material may vary. The parameters G_∞ and G_0 which determine ΔG are sometimes called, respectively, the unrelaxed modulus, $G_{un} = G_\infty$, and the relaxed modulus, $G_r = G_0$. The unrelaxed modulus G_{un} corresponds to such a relationship between stress and strain at which the changes in these quantities occur so rapidly that no relaxation has a chance to take place. This can be realized either at very high frequencies (at $\omega \rightarrow \infty$) or, which is more realistic, at very low temperatures (at $\tau \rightarrow \infty$). The expressions for the sound velocity and

the acoustic absorption coefficient for the standard linear solid may be written as follows:

$$c^2 = c_0^2 + c_1^2 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (7.56)$$

$$\frac{\alpha \lambda}{2\pi} = \frac{1}{2} \frac{c_1^2}{c^2} \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (7.57)$$

where $c_0^2 = G_0/\rho$ and $c_1^2 = G_1/\rho$.

Formulas (7.56) and (7.57) describe the propagation of shear waves in the standard linear solid. Obviously, it is not difficult to find analogous expressions for the velocity and absorption coefficient of longitudinal waves propagating in the standard linear viscoelastic solid.

Let us consider another rheological model—a rheological model which is equivalent, in some respects, to the standard linear solid. Let the instantaneous compliance in formula (7.43) be $J_\infty = 1/G_\infty \neq 0$. Then, setting all the compliances J_j , except one, equal to zero, we obtain:

$$\frac{1}{G^*} = J^* = \frac{1}{G_\infty} + \frac{1}{G_1} \frac{1}{1 + \omega^2 \tau^2} - i \frac{1}{G_1} \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (7.58)$$

Expression (7.58) is satisfied by a single Kelvin-Voigt model connected in series with one more spring (Fig. 7.4). The sound velocity corresponding to this case may be represented in the following form:

$$\frac{1}{c^2} = \frac{1}{c_\infty^2} + \frac{1}{c_1^2} \frac{1}{1 + \omega^2 \tau^2} \quad (7.59)$$

In the limiting case of low frequencies (at $\omega \rightarrow 0$) $1/c_0^2 = 1/c_\infty^2 + 1/c_1^2$, from which $c_0^2 = c_1^2/(1 + c_1^2/c_\infty^2)$. In the other limiting case of high frequencies (at $\omega \rightarrow \infty$) $c = c_\infty$.

In concluding, it should be noted that attempts have been repeatedly made to use the simple Maxwell or Kelvin-Voigt model for describing the dynamic viscoelastic properties of polymeric materials. From what has been said above it follows that such an approach is fundamentally incorrect since formulas (7.45) and (7.49) fail to describe, even qualitatively, the dynamic viscoelastic properties of polymers. In order to estimate quantitatively the viscoelastic behaviour of polymers in certain cases, one can make use of the standard linear solid or the model shown in Fig. 7.4. The latter two models can be employed only for describing a single relaxation process, in which the relaxation time distribution can be, at a first (very crude) approximation replaced by a single averaged ("effective") relaxation time. Expressions (7.50) through (7.59) provide a correct qualitative description of the dynamic viscoelastic and acoustical properties of polymers: they indicate the dispersion (frequency dependence) of the dynamic elastic modulus (or the sound

velocity dispersion); they lead to finite values of the dynamic modulus in the case of both low frequencies ($\omega \rightarrow 0$) and high frequencies ($\omega \rightarrow \infty$); they show that for each relaxation process there must occur a peak in the frequency dependence of $\tan \delta$.

The most detailed information on the viscoelastic behaviour of polymers can be obtained if only one takes account of the relaxation-time distribution, i.e., if the concepts of relaxation time spectra are used.

The most general method of describing the viscoelastic behaviour of polymers is evidently the method based on the solution of the Boltzmann-Volterra after-effect equation. This method, however, is used in very rare cases for describing the dynamic viscoelastic and acoustical properties of polymers.

7.3. Dependence of Viscoelastic Properties on Frequency and Temperature

The dependence of the dynamic elastic modulus, the sound velocity and the acoustic absorption coefficient on frequency is determined by the expressions given above.

Let us consider one of the simplest cases—the frequency dependence of the quantities G' , G'' , $\tan \delta$ and c for a viscoelastic material that can be depicted by the model of the standard linear solid. Figure 7.5 shows the frequency dependence of the above-indicated parameters as calculated from formulas (7.52) through (7.56).

The features of the functions $G' = f_1(\log \omega)$, $c = f_2(\log \omega)$, $G'' = f_3(\log \omega)$ and $\tan \delta = f_4(\log \omega)$ that deserve attention are as follows. First, it is obvious that the dynamic modulus has a point of inflection at $\omega = 1/\tau$ ($\omega\tau = 1$), while the point of inflection in the $c = f_2(\log \omega)$ curve corresponds to a lower frequency. Second, the curve of G'' versus $\log \omega$ has a peak at $\omega\tau = 1$, while $\tan \delta$ passes through a maximum at a lower frequency. The latter circumstance is associated with the fact that formula (7.54) for $\tan \delta$ contains the relaxation time τ_1 , which is different from the relaxation time τ in expression (7.53) for G'' . Since the conditions for the occurrence of the G'' and $\tan \delta$ peaks are the relations $\omega\tau = 1$ and $\omega_1\tau_1 = 1$ and since (as has already been shown) $\tau_1 \geq \tau$, it becomes clear that a peak in the curve of $\tan \delta$ versus frequency must appear at lower frequencies than the corresponding peak in the curve of G'' versus $\log \omega$.

Thus, from the shift of the peaks in the experimentally found curves of $G'' = f(\omega)$ and $\tan \delta = f(\omega)$ one can determine the amount of dispersion of the dynamic modulus if the values of τ_1 and τ are known. In accordance with formula (7.55) the dispersion of the

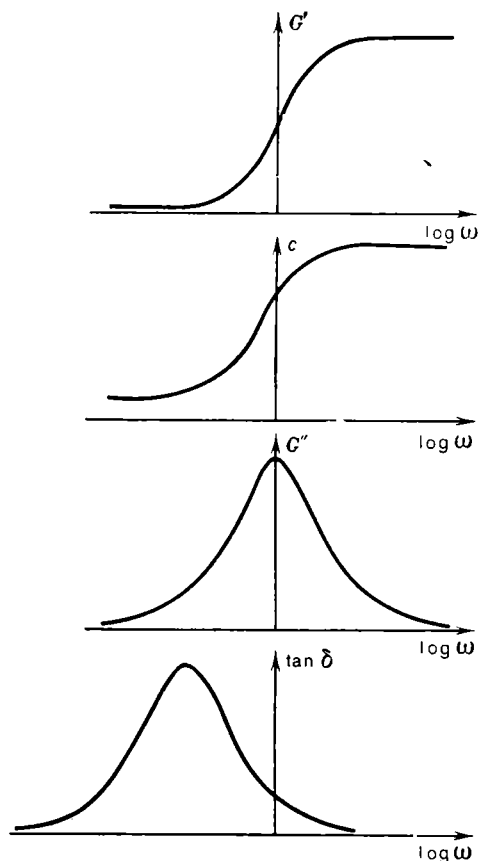


Fig. 7.5. The theoretical frequency dependence of the quantities G' , c , G'' and $\tan \delta$ for a viscoelastic material, which may be described by the model of the standard linear viscoelastic body.

modulus ΔG depends on τ_1/τ , or

$$\Delta G = \frac{(\tau_1/\tau)^2 - 1}{\tau_1/\tau}$$

In accordance with formula (7.55), the height of the $\tan \delta$ peak will also be the greater, the more strongly the corresponding peaks in the curves of $G'' = f(\omega)$ and $\tan \delta = f(\omega)$ are shifted relative to each other. It is very difficult to compare the frequency dependences predicted by theory with experimental data for polymers, since there are almost no works, the authors of which have succeeded in studying the frequency dependence of the viscoelastic properties of polymers over a sufficiently wide range of frequencies. This is because acoustical investigations of polymers in a wide frequency range can only be carried out by using several different methods and, accordingly, samples of different shapes and sizes. In this case, samples usually differ from one another by the method of preparation and by their previous thermal history.

Fig. 7.6. The experimental frequency dependence of E' (1) and $\tan \delta$ (2) for polycapramide (after Waterman).

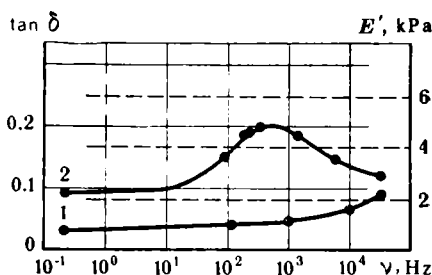


Figure 7.6 presents the results of measurements of E' and $\tan \delta$ in Nylon 6 (polycapramide) carried out by Waterman (6). Though these measurements cover five decades of frequency, Waterman failed to obtain the full dispersion curve.

In order to describe the temperature dependence of the viscoelastic properties of polymers, one can use formulas (7.52) through (7.54), (7.56) and (7.57). Though the temperature does not figure in them explicitly, it is nevertheless well known that the relaxation time depends strongly on temperature: it decreases with increasing temperature. There exist various types of the dependence of τ on temperature. The most frequently used relation is the exponential form of the temperature dependence of τ which is described by an equation of the type

$$\tau = Ae^{U/RT} \quad (7.60)$$

where A is a certain constant; U is the energy of activation; R is the universal gas constant; T is the temperature.

Other types of the temperature dependence of τ are sometimes used. Thus, for example, substituting $\tau = f(T)$ into formulas (7.52) through (7.57), one can obtain expressions for the temperature dependence of the dynamic viscoelastic properties of polymers. The results of such calculations from formulas (7.52) through (7.56) for a viscoelastic material, which corresponds to the model of the standard linear solid, are shown in Fig. 7.7. As might be expected, the curves of G' and c versus temperature are the mirror image of the curves of G' and c versus frequency. The quantities G' and c increase with increasing frequency ω , tending to the maximum values G'_∞ and c_∞ , but as the temperature is raised G' and c fall off, tending to the values G'_0 and c_0 . Since τ_1 , which figures in formula (7.54) for $\tan \delta$ is larger than τ in expression (7.53) for G'' , it follows that on the temperature scale the $\tan \delta$ peak occurs at higher temperatures than does the corresponding G'' peak. In fact, the $\tan \delta$ peak appears provided that $\omega_1 \tau_1 = 1$ and the G'' peak occurs at $\omega \tau = 1$. If measurements are carried out at a single frequency, $\tau_1 = \tau$.

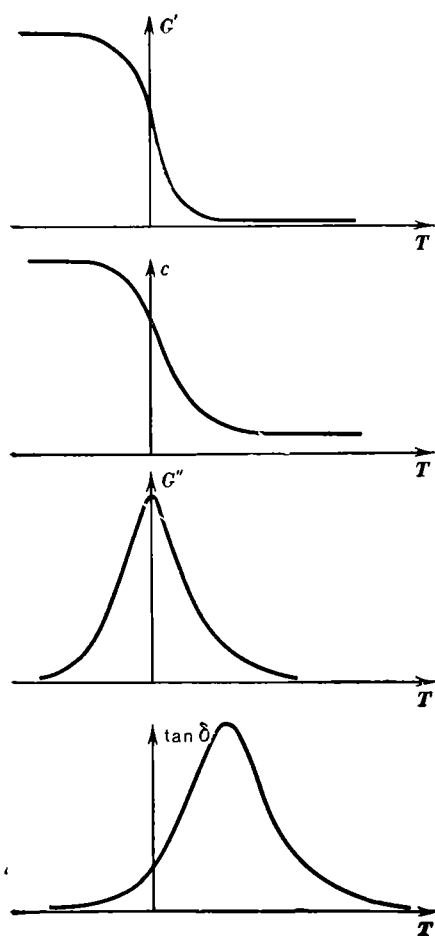


Fig. 7.7. The temperature dependence of the quantities G' , c , G'' and $\tan \delta$ for a viscoelastic material, which corresponds to the standard linear solid.

It has been shown above that $\tau_1 = \tau \cdot \sqrt{G_\infty/G_0}$. Using the Arrhenius equation, we can write:

$$\sqrt{G_\infty/G_0} \cdot \tau_0 e^{U/RT_1} = \tau_0 e^{U/RT}$$

Since $\sqrt{G_\infty/G_0} \geq 1$, it evidently follows that the above equality will be satisfied provided only that $T_1 \geq T$. Thus, the use of even such a simple model as the standard linear solid for describing the temperature dependence of acoustical properties enables one to account for a very interesting experimental fact—the appearance, at different temperatures, of the $\tan \delta$ and G'' and J'' peaks corresponding to a single relaxation process. As a matter of fact, it has long been found that the $G'' = f(T)$, $\tan \delta = f(T)$ and $J'' = f(T)$ curves calculated from the same experimental data have peaks corresponding to the same relaxation process at different temperatures. Various reasonings have been put forward concerning the causes of

this effect, but no correct explanation has been given. The thorough experiments carried out by Crissman and Passaglia (7) and devoted to the investigation of polytrifluorochloroethylene have shown that the temperature at which a loss peak is observed depends on the choice of the dynamic viscoelastic function. It has been found that the G'' peak appears first in the temperature dependence; at a higher temperature the $\tan \delta$ peak is attained, and finally at the highest temperature the J'' peak occurs. This disposition of transition temperatures agrees well with the results of theoretical calculations made from formulas (7.52) through (7.56).

It should be noted that while the theoretically calculated curves of G' , G'' and $\tan \delta$ versus temperature agree, at least qualitatively, with the corresponding experimental curves, the curve of c versus temperature does not reflect, even qualitatively, the character of the temperature dependence of the sound velocity. Indeed, it has been shown in a number of experimental investigations (see, for example, ref. 4) that the velocity of sound is linearly dependent on temperature and only when the nature of molecular mobility is changed does the temperature coefficient of sound velocity undergo a discontinuous change. It has also been established that the temperature transition detected in such a way is usually observed at lower temperatures than the corresponding $\tan \delta$ peak. A typical temperature dependence of sound velocity for polytetrafluoroethylene is shown in Fig. 3.2.

As has been shown above, the main viscoelastic properties of polymers can be accounted for with the aid of relaxation theory.

As has already been said, relaxation is a process of transition of the system to a state of thermodynamic equilibrium. Suppose that the system is brought out of the state of thermodynamic equilibrium under the influence of external forces. After the load is removed the system left to its own devices will return to the state of thermodynamic equilibrium. This transition of the system to thermodynamic equilibrium under the influence of internal forces is what we call relaxation, and the time required for this process to be accomplished is called the relaxation time.

The passage to the state of thermodynamic equilibrium in polymers is accomplished due to the various types of molecular motion. To each type of molecular motion there corresponds a definite relaxation process characterized by its own relaxation time. In order to observe and investigate a relaxation process in polymers and the corresponding type of molecular motion, it is necessary that the loading time (or the observation time) be commensurate with the relaxation time. Hence, for relaxation processes to be studied by acoustic methods (and this is one of the most widely used methods), it is necessary that the period of sound vibrations be of the same order of magnitude as the relaxation time of the polymer. Let us consider

a linear amorphous polymer in the rubbery state. In this case the number of possible conformations that each of the macromolecules can adopt is sufficiently large, and the diverse types of molecular motion are realized in the polymer. Suppose that sound vibrations are propagating in this polymer; the frequency of these vibrations can be varied within wide limits. If the frequency of sound vibrations is very low, i.e., the period of sound vibrations is very large as compared with the relaxation time of the largest kinetic units of macromolecules, the energy of acoustic vibrations received by the volume element of the polymer per period of vibration will be rapidly redistributed throughout the entire volume of the polymer due to segmental mobility of the micro-Brownian type (the diffusion of macromolecular segments). In this case the process of energy dissipation is a quasi-equilibrium process, the mechanical losses are not large and the polymer restores quickly its dimensions and shape after the external load is removed. Naturally, the dynamic elastic modulus of the polymer (and also the velocity of sound in it) will be very small, i.e., of the same order as the modulus of a liquid.

As the vibrational frequency is increased (the period of vibration T is reduced) and ω increases and tends to $1/\tau$ (but $\omega\tau < 1$), the dissipation of the energy of sound vibrations will also increase, since the time during which the energy dissipation will take place (due to segmental diffusion) will increasingly approach one period. There will probably be such large and "inconveniently" arranged segments which will have no chance during one period of vibration to take part in the transfer of energy to their neighbours. This means that they will behave as rather stiff chain units towards the external forces. All this will lead to an increase in the "apparent" stiffness of the polymer and, hence, to an increase in the dynamic modulus and sound velocity with increasing frequency. Thus, if $T/\tau > 1$, an increase in the vibrational frequency must lead to an increase in the dynamic elastic modulus, sound velocity and energy dissipation (to an increase in $\tan \delta$).

As the frequency is further increased (the period of vibration is reduced) the proportion of segments that will not be able to transfer the extra energy of sound vibrations to their neighbours per period of vibration will increase and more and more segments will thus become rigid. This will result in a further increase in the dynamic elastic modulus and sound velocity with increasing frequency, but the rate of increase of energy dissipation (increase of $\tan \delta$) will be retarded since more and more segments will have no chance to convert the energy received into heat during one period of sound vibrations.

If the vibration frequency is further increased, i.e., if the ratio T/τ is diminished (and $\omega\tau$ is increased), more and more segments will be out and when the period of sound vibrations becomes com-

mensurate with the relaxation time ($\omega\tau \approx 1$), the mechanical loss tangent (the loss factor) $\tan \delta$ will pass through a maximum, and as the frequency is increased further the mechanical losses in the polymer will begin to diminish. The dynamic modulus and the velocity of sound will increase.

Finally, if the frequency increases still further and the period of sound vibrations T becomes much shorter than the relaxation time τ associated with segmental mobility (i.e., at $\omega\tau \gg 1$) and when almost all the segments will have chance to transfer the "extra" acoustic energy received to their neighbours during time T , the propagation of vibrations will again become a quasi-equilibrium process. The dissipation of the vibrational energy will here be very small and the dynamic elastic modulus will reach a certain limiting value 3 or 4 orders of magnitude higher than the elastic modulus measured at low frequencies. Thus, at sufficiently high vibrational frequencies the polymer in the rubbery state behaves as if it were in the glassy state. This is what we call mechanical glass transition; the concept of this phenomenon was introduced by Bartenev.

With a further increase in frequency, there will occur relaxation processes due to the mobility of smaller kinetic units of the polymeric chains which are characterized by shorter relaxation times. Eventually, at very high vibration frequencies almost all kinetic macromolecular units will become "frozen". In the absence of quantum effects a situation may occur when the condition $\omega\tau_j \gg 1$ is fulfilled for any τ_j . In this case the entire relaxation spectrum of the polymer will be "frozen".

Thus, the values of the mechanical loss tangent and sound velocity dispersion for each particular relaxation process are determined by the ratio T/τ . The change of the frequency (and, hence, of the period of vibration) at constant temperature is only one of the methods by which the ratio T/τ can be changed. Naturally, all the above reasonings will remain valid if the ratio T/τ is changed due to a change in relaxation time τ , i.e., a change in temperature. Since the sound velocity increases and the loss tangent passes through a maximum as the ratio T/τ diminishes, it evidently follows that this can be achieved not only by increasing the frequency (reducing the period T) of sound vibration at constant temperature but also by increasing τ (by lowering the temperature) at constant frequency. Thus, increasing the frequency and lowering the temperature has the same effect on the dynamic viscoelastic properties of polymers. It should be noted that the second method of investigating relaxation processes is more easily realized experimentally and it is quite natural that the principal method of investigating relaxation phenomena taking place in polymers is to study the temperature dependences of the viscoelastic properties at one or more frequencies.

7.4. Acoustic Spectroscopy

The main parameters that characterize the dynamic viscoelastic properties of polymers are the components of the complex modulus (the storage modulus and the loss modulus) and also the loss tangent (the loss factor) $\tan \delta$. The dynamic viscoelastic properties of polymers are usually studied by using low-frequency sound vibrations and may be treated as low-frequency acoustical properties.

The parameters characterizing the dynamic viscoelastic properties of polymers are mainly governed by two factors: the chemical structure and the specific features of the supermolecular structure. There exists a clear-cut correlation between chemical structure, physical structure, molecular mobility and such parameters as the sound velocity, the acoustic absorption coefficient, the components of the complex elastic modulus. The values and the mode of variation of the dynamic elastic moduli and sound velocity with frequency (or temperature) are determined by the bond energy of the main-chain atoms and the interaction energy of the units of neighbouring polymeric chains, i.e., the intermolecular interaction energy.

In various acoustic experiments both types of interaction manifest themselves very specifically. For example, the sound velocity measured in an oriented polymer fibre or film, whose macromolecular conformations are close to linear, is mainly determined by the energy of interaction of the main-chain atoms and may reach values of the order of 10^6 cm/s, by far exceeding the sound velocity in unoriented metals. At the same time, the sound velocity measured in an uniaxially oriented film not along but perpendicular to the axis of orientation is largely determined by the intermolecular interaction energy and coincides, in order of magnitude (1.2 to 1.5) $\times 10^5$ cm/s, with the sound velocity in most organic liquids.

The effect of the nature of intermolecular interaction on the dynamic elastic moduli of the same polymer in different physical states is even more pronounced. In the glassy state, where the intermolecular interaction is sufficiently great, the dynamic elastic moduli of most linear amorphous polymers have values of the order of 10^3 MPa. In the rubbery state, where the energy of intermolecular interaction is substantially lower, the dynamic elastic moduli of the same polymers range from 0.1 to 1 MPa.

Since the changes in the nature of the supermolecular structure of macromolecules, the composition of the components in compounded polymers and in the temperature of the polymer eventually lead to a change in the effectiveness of intermolecular interaction, it is clear that all these factors have a very appreciable effect on the magnitude and nature of the dynamic elastic modulus and sound velocity. Thus, the storage modulus and sound velocity enable one to obtain information of two kinds: first, information concerning

the most important mechanical (deformation) properties of polymers and, second, information about the constitution, structure and state of the polymer. Besides, these parameters allow one to study relaxation processes which are responsible for the most important physico-mechanical properties of polymers.

The loss modulus, the loss tangent and the acoustic absorption coefficient are mainly determined by the type and intensity of molecular motion. The "unfreezing" of almost each new type of molecular motion leads to the appearance of peaks in the temperature or frequency dependence of the loss factor. Thus, molecular mobility, whose characteristics are the loss modulus and the acoustic absorption coefficient, depends greatly on the chemical structure of the polymer.

The change of the intermolecular interaction energy has an effect not only on molecular motion in polymers but also on the value and nature of mechanical losses.

When the frequency of acoustic vibrations or temperature are changed within wide limits, the dynamic mechanical (viscoelastic) properties of polymers undergo considerable changes caused by the occurrence of relaxation processes associated with various types of molecular motion. The nature of molecular motion is determined by the chemical and physical structure of the polymer. On the other hand, the most important physical properties of polymers depend on the intensity and specific features of relaxation processes and, hence, on the type of molecular motion.

One of the principal methods of investigation of molecular motion in polymers is to study the temperature dependences of the parameters characterizing the dynamic mechanical properties, especially the temperature dependences of the storage modulus, sound velocity, $\tan \delta$ and the loss modulus.

If the polymer is cooled down to a very low temperature at which no molecular motion is present (this cannot be attained in all cases since in some polymers the molecular mobility is still possible even at 0 K) and the parameters indicated above are measured with the temperature being gradually raised, the various types of molecular motion in the polymer will begin to be successively unfrozen. In this process, each type of molecular motion will leave its imprint on the $\tan \delta = f(T)$, $G' = f(T)$, $c = f(T)$, and $G'' = f(T)$ graphs. The temperature dependences of these parameters are, as it were, snapshots giving information on the various kinds of molecular motion that can occur in the polymer and also on its structure. Each type of molecular motion is usually associated with a certain definite relaxation process caused by the given type of molecular mobility.

At very low temperatures (at $T \rightarrow 0$ K) the relaxation times of almost all relaxation processes are very large, and for them the

condition $\omega\tau \gg 1$ is fulfilled. Since at a first approximation τ is proportional to $\exp(U/RT)$, it follows that all relaxation times decrease with increasing temperature and when the condition $\omega\tau = 1$ is fulfilled for a particular relaxation process, a maximum appears in the temperature dependence of $\tan \delta$ or G'' . Under the same conditions the storage modulus is decreased.

When measurements are carried out at a constant frequency over a wide temperature range, it is possible to reveal all the relaxation processes, characteristic of a given polymer, which are associated with various types of molecular mobility that can be realized in the polymer. The occurrence of each new type of molecular mobility, which leads to substantial changes in the temperature dependence of the dynamic mechanical properties, is usually treated as a temperature transition. The temperature transitions can be determined from the peaks in the temperature dependence of the loss modulus or loss compliance and $\tan \delta$, from a change in the temperature coefficient of the sound velocity (4) and from the point of inflection in the temperature dependence of the storage modulus.

It has been explained above why the peaks of the various viscoelastic functions for the same relaxation process appear to be located at different temperatures. Note that to the lowest temperature there always corresponds the temperature transition recognized by a change in the temperature coefficient of the sound velocity. This is not surprising since this transition corresponds to the temperature above which a definite type of molecular mobility becomes unfrozen.

The temperature transitions that occur in amorphous polymers are relaxational in character. In crystalline polymers, thermodynamic phase transitions are also classified as temperature transitions. If the temperature transition is associated with a relaxation process, then it must shift towards higher temperatures as the frequency is increased. The transition temperatures measured by various investigators on a polymer at the same frequencies and with the same type of deformation used are, as a rule, consistent. Most frequently, these temperatures are determined from the position of the $\tan \delta$ peak. The relaxation peak in the temperature dependence of $\tan \delta$ occurs when $\omega\tau = 1$. So, when a peak in the curve of $\tan \delta$ versus temperature is detected, it is possible not only to establish the transition temperature but also to determine the relaxation time $\tau = 1/\omega$ of the corresponding relaxation process. Since for each molecular mechanism in the polymer there is a certain distribution of relaxation times, it follows that the relaxation time τ found in this way is a certain "effective" relaxation time. Such replacement of a set of relaxation processes corresponding to a single molecular mechanism by a single process is used fairly often.

If measurements are carried out at several frequencies, the $\tan \delta$ peak corresponding to a single relaxation process will be shifted

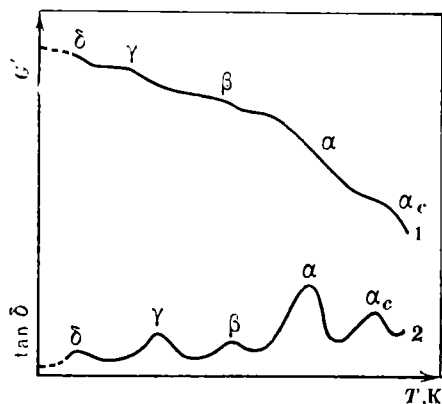


Fig. 7.8. Temperature transitions in amorphous-crystalline polymers: 1— G' ; 2— $\tan \delta$; see the text for explanations.

with increasing frequency towards higher temperatures. As a matter of fact, for each frequency ω_i the loss factor $\tan \delta$ will have a peak provided that $\omega_i \tau_i = 1$. If $\omega_{i+1} > \omega_i$, then it is evident that from the condition of the appearance of the $\tan \delta$ peak it follows that $\tau_i > \tau_{i+1}$. Hence, to the peak measured at a higher frequency there will correspond a shorter relaxation time. Since we are speaking of one and the same relaxation process, it follows that this is possible only at a higher temperature. By plotting the dependence of $\log f_m$ on $1/T_m$ (where f_m is the frequency of sound vibrations at which there is observed a $\tan \delta$ peak, and T_m is the temperature at which this peak occurs), one can obtain information about the nature of the relaxation process. If the plot of $\log f_m$ against $1/T_m$ is a straight line, this means that the temperature dependence of the relaxation process can be described by the Arrhenius equation:

$$\tau = \tau_0 e^{U/RT}$$

where $\tau_0 = 10^{-12}$ to 10^{-14} s; U is the activation energy of the relaxation process.

In such a case, according to the ideas of Frenkel and Eyring, the relaxation time is determined by the probability of the jump of a kinetic unit of the macromolecule responsible for a given relaxation process from one position to another through a potential energy barrier. In many cases, the Arrhenius equation is the basis for the calculation of the energy of activation, which can be found by various methods (4).

The general diagram of temperature transitions in amorphous-crystalline polymers is given in Fig. 7.8. Usually, temperature transitions, beginning from the highest-temperature transition, are labelled by the Greek letters α , β , γ and δ . Relaxation processes that occur with fall of temperature are denoted by the same letters.

The highest-temperature α_c -transition shown in Fig. 7.8 may be a multiplet transition associated with the movement of polymeric

chains in crystalline regions. According to the model proposed by Hoffmann, Williams and Passaglia (8), this temperature transition is connected with the motion of folds and with the reorientation of polymeric chains. The apparent energy of activation of a relaxation process of this type ranges from 167 to 418 kJ/mole.

The dynamic mechanical properties of crystalline polymers are strongly influenced by the relaxation process due to the glass transition of the amorphous layer (the α_{am} -relaxation). In highly crystalline polymers this relaxation process degenerates and can be barely observed in this case in the temperature dependences of G' , G'' , and $\tan \delta$.

With amorphous polymers this relaxation process is dominant, being associated with the transition from the glassy state to the rubbery state (or vice versa). This thermal transition is due to the unfreezing of segmental mobility of the micro-Brownian type and leads to the most marked change in the dynamic modulus of amorphous polymers (from 10^3 MPa in the glassy state to 0.1 MPa in the rubbery state) and to the appearance of the most intense loss peak. Molecular mobility is realized in this case due to large kinetic units in the main chain of the polymer. The temperature transition corresponding to the α_{am} -relaxation can be singlet or multiplet (4, 9). The dependence of $\log f_m$ on $1/T_m$ is most often nonlinear in character in the case of α_{am} -relaxation and $\log f_m$ diminishes with increasing $1/T_m$. This means that the plot of $\log \tau_m$ against $1/T_m$ is also nonlinear and, hence, the energy of activation depends on temperature. It is for this reason that the quantity U found from the Arrhenius equation is called the temperature coefficient of the relaxation time or the "apparent" energy of activation.

The value of the "apparent" activation energy for the α_{am} -relaxation process provoked by the segmental mobility of main chains ranges from 84 to 840 kJ/mole. These high values of apparent activation energy, which appears to be dependent on the temperature at that, point to the non-Arrhenius character of the temperature dependence of the relaxation time and are accounted for by the nature of the glassy state of polymers. The large values of activation energy which are so characteristic of the α_{am} -relaxation process associated with segmental mobility are sometimes ascribed to the cooperative motion of the segments of polymeric chains. In this case the energy of activation should be expected to diminish with increasing temperature. It is exactly this dependence of U on temperature that has been found by Bartenev and Lukyanov (10) for the glassy region and by Shishkin (11) for the rubbery region.

Nevertheless, the exceedingly high values of activation energy and its strong dependence on temperature indicate that the Arrhenius equation in its simplest form is probably inapplicable near T_g . In this connection, Fox and Flory presume that molecular mobility

(and, hence, the relaxation time) near T_g is largely governed by the free volume v_f . It is assumed that the probability of a jump is determined not by the velocity with which a segment can overcome the energy barrier separating it from the adjacent hole but by the probability that there is a free volume large enough for the segment to move into.

The idea advanced by Fox and Flory has been formulated in the well-known Williams-Landel-Ferry (WLF) equation (1):

$$\log a_T = -\frac{c_1(T-T_0)}{c_2+T-T_0} \quad (7.61)$$

where $a_T = \tau/\tau_0$ is the ratio of the relaxation time at a particular temperature T to the relaxation time at a certain reference temperature T_0 (it is called the shift factor); c_1 and c_2 are constants.

Later Bueche (12) derived this formula, using the free-volume theory. The main idea of Bueche is that the molecules or their segments cannot move independently near T_g . If one of the segments is moving, the segments that surround it must take part in this motion to make it possible. A jumping unit is defined by Bueche as a certain group of segments or molecules taking part in the cooperative motion. It has thus been shown that the cooperativity of segmental motion allows the non-Arrhenius temperature dependence of the relaxation time to be accounted for.

It has however been found that the WLF equation holds only over a narrow temperature range, from T_g to $T_g + 50$. At higher temperatures the relaxation time obeys the Arrhenius equation, this being associated with the violation of cooperativity resulting from the weakening of the intermolecular interaction. In the glassy state (below T_g) the relaxation time again becomes dependent on temperature in accordance with the Arrhenius equation.

Macedo and Litovitz (13) made an attempt to take account of the contribution of both the free volume and the energy of activation to the temperature dependence of viscosity and relaxation time near T_g , i.e., they tried to make use of both the absolute rate theory and the free-volume theory. They proceeded from the assumption of the quasi-crystalline structure of liquids and presumed that a molecule in a liquid is vibrating in the equilibrium position until, first, it acquires a sufficient amount of energy to overcome the attractive forces that hold it in its position near its neighbours and, second, until there is a hole nearby into which it can jump. The use of these assumptions leads to the following formula:

$$\tau = \tau_0 \exp \left[\gamma \frac{V_0}{V_f} + \frac{U}{RT} \right] \quad (7.62)$$

where γ is a numerical coefficient; V_f is the free volume; V_0 is the occupied volume.

Expression (7.62) enables one to describe the temperature dependence of the relaxation time both above and below T_g . Formula (7.62), however, has barely been applied for the investigation of polymers.

The next temperature transition, which takes place at lower temperatures is known as the β -transition (the β -relaxation). This thermal transition, which is located in the region of the glassy state, usually includes relaxation processes associated with the motion of side groups or small units of the main chain. In view of this, by the β -relaxation we mean the various temperature transitions. For example, while the β -relaxation occurring in polymethyl methacrylate is understood to mean a process associated with the reorientational motion of side chains (14), with polytrifluorochloroethylene the β -relaxation is a process provoked by the glass transition of the amorphous regions (8), and in the case of crystalline polytetrafluoroethylene it is a phase transition, which leads to a change in the type of unit cell of the polymer. It has been suggested (15) that only the processes attributable to the motion of side groups be included in the category of β -relaxations. The apparent energy of activation for β -relaxations is 63-167 kJ/mole.

At lower temperatures, only those thermal transitions occur which are provoked by small kinetic units of the main or side chains of the polymer, these chains consisting of several successively linked carbon atoms. Such temperature transitions (γ -relaxations) are often connected with the movement of four or more CH_2 or CF_2 groups. In crystalline polymers one observes the phenomenon of γ -relaxation attributable to the reorientational motion of chain ends in crystallites and the presence of defects in them (γ_{cr} -relaxation) (8) and also to the mobility of several aliphatic carbon atoms in the amorphous regions (γ_{am} -relaxation).

At very low temperatures, there are observed temperature transitions associated with the mobility of end groups and individual atomic groups in branchings (δ -relaxation). An example of δ -relaxation is the motion of the phenyl groups in polystyrene or the motion of the methyl groups in polypropylene at low temperatures. The δ -relaxation process may be of a complex multiplet nature. The activation energy for δ -relaxations ranges from 17 to 42 kJ/mole; in the case of γ -relaxations the activation energy $U = 29$ to 84 kJ/mole.

The β -, γ - and δ -relaxation processes that occur in amorphous polymers in the glassy region are, as a rule, in satisfactory agreement with the conception that the elementary jump of a kinetic unit of the macromolecule is non-cooperative and occurs independently of the other kinetic units of the same type and is confined to a small volume.

The occurrence of the various temperature transitions in a particular polymer depends on its chemical and physical structure.

It should be noted that the entire gamut of relaxation processes

taking place in crystalline and amorphous polymers cannot be reduced to the relaxation mechanisms described above, these not even being self-evident themselves. It is, however, quite obvious that the molecular mechanism of relaxation processes in crystalline and amorphous polymers is largely governed by their supermolecular organization.

Thus, the dynamic viscoelastic properties of polymers are strongly dependent on their chemical and physical structure. This is reflected in the temperature dependence of the loss modulus, $\tan \delta$, the acoustic absorption coefficient, the sound velocity, and the dynamic modulus (the storage modulus). It may be asserted that there are no two polymers of different chemical structure whose temperature dependences of these parameters are identical. This has recently led to the development of the acoustic spectroscopy of polymeric materials, the main task of which is to establish the relationship between chemical and physical structure and composition, on the one hand, and the acoustic parameters (including the parameters that characterize the mechanical properties), on the other.

Another objective of acoustic spectroscopy is to obtain information on the chemical and physical structure and composition of polymeric materials on the basis of the study of the temperature or frequency dependences of the acoustic parameters.

The salient features of the acoustic spectroscopy of polymers are manifested in a specifically individual manner in the investigation of the dynamic viscoelastic properties of polymers over a wide range of temperatures and frequencies.

7.5. Dependence of the Acoustical Parameters of Polymers on Their Structure

7.5.1. Crystalline Polymers

One of the main parameters that characterize the crystalline structure of polymers is the degree of crystallinity α defined by formula (2.12). The magnitude of α has a substantial effect on the viscoelastic properties of crystalline polymers. As a result, the glass-transition temperature of the amorphous regions, the intensity of the relaxation peaks, the values of the dynamic elastic moduli and sound velocity are, as a rule, appreciably dependent on the degree of crystallinity.

Usually, the glass temperature of a poorly crystallized polymer ($\alpha \approx 0.1$) practically coincides with the glass temperature of the fully amorphous sample. As the degree of crystallinity increases the glass temperature of the amorphous regions most often shifts towards higher temperatures. This shift of T_g can be explained within the framework of the Adam-Gibbs theory (see Chapter 3):

the degree of chain orientation in the amorphous regions gradually increases with increasing crystallinity. Such a dependence of T_g on α is encountered most frequently and is considered to be "normal". It has been found (4) that in some polymers (say, in polyethylene terephthalate) over a certain range of α values there is observed an "anomalous" dependence of T_g on the degree of crystallinity. In such cases, T_g falls off with increasing crystallinity. It may be presumed that the dependence of the glass-transition temperature of the amorphous layer on the degree of crystallinity is determined by two factors: (1) the nature of the supermolecular structure of polymeric chains in the crystalline regions and (2) the condition of the amorphous layer. Naturally, all these factors also have an effect on the position and intensity of the loss peaks.

The measurements of loss peaks on samples of the same polymer with different degrees of crystallinity are ordinarily used to elucidate the mechanism of relaxation processes. Use is most often made of the dependence of $\tan \delta$ on temperature. If the height of the loss ($\tan \delta$) peak (or the area under this peak in the curve of $\tan \delta$ versus temperature) increases with increasing crystallinity, it is presumed that the relaxation peak is due to the processes occurring in the crystalline regions. If the height of the peak in the curve of $\tan \delta$ versus temperature diminishes with increasing α , it is supposed that this process takes place in the amorphous regions. Usually, the $\tan \delta$ peak corresponding to the unfreezing of segmental motion in amorphous regions (the α_{am} -relaxation) becomes less and less intense with increasing degree of crystallinity and is completely degenerated in highly crystalline samples (at $\alpha \rightarrow 1$). The position of the α_{am} -peak on the temperature scale usually depends on α in the same way as does T_g .

It is sometimes believed that more reliable data on the nature of relaxation peaks can be obtained by studying the effect of crystallinity on the intensity and position of the maxima of the functions $E'' = f(T)$ and $J'' = f(T)$. At first glance, the dependence of the peaks of these functions on crystallinity must be the same as in the case of the peaks in the curve of $\tan \delta$ versus temperature. However, Gray and McCrum (16) have found that for the relaxation process associated with the glass transition of polytrifluorochloroethylene E''_{max} increases with increasing degree of crystallinity, while J''_{max} decreases under the same conditions. Such a dependence of the maxima of the various viscoelastic functions attributable to the same relaxation process on the degree of crystallinity could not be explained for a long time and seemed strange and abnormal.

It is customarily thought that the dynamic elastic modulus and the sound velocity in polymers increase with increasing crystallinity. This dependence is most distinctly manifested when acoustic measurements are carried out at temperatures higher than the glass-

transition temperature of the amorphous layer. An increase in the sound velocity and the dynamic elastic modulus with increasing degree of crystallinity is associated with the intensification of intermolecular interaction in the polymer as a result of an increase in the content of ordered crystalline regions. It is clear that this effect must be observed in the most distinct manner if the amorphous regions of the polymer are in the rubbery state, in which the intermolecular interaction is weak.

It is usually believed that in the glassy state (below the glass-transition temperature of the amorphous layer) the modulus of elasticity and the sound velocity are independent of the degree of crystallinity, since the densities of crystallites and amorphous regions below T_g must not practically differ. A clear-cut dependence of the sound velocity and the dynamic modulus on the degree of crystallinity near room temperature (E' and c are both proportional to κ) is observed for such polymers as polyethylene (4) and polytetrafluoroethylene with their amorphous regions being in the rubbery state.

It has been shown experimentally (4) that the dynamic elastic modulus of a number of crystalline polymers (polytrifluorochloroethylene, polycapramide, polyethylene) in the low-temperature region decreases with increasing degree of crystallinity.

It can be shown that this anomalous effect of the degree of crystallinity on the acoustical properties of polymers can be explained on the basis of the phenomenological relaxation theory (17, 18).

In order to account for a number of anomalies in the behaviour of the acoustic parameters brought about by a change in crystallinity, let us employ the results obtained in the preceding sections.

In the case of a continuous retardation-time spectrum the expression for the complex compliance can be written in the form:

$$J^* = J' - iJ'' = \frac{1}{E_q} + \int_0^\infty \frac{L(\tau) d\tau}{1 + \omega^2 \tau^2} - i \int_0^\infty \frac{\omega \tau L(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (7.63)$$

where $E_q = E_\infty$. Suppose that the relaxation processes that occur in a crystalline polymer are regarded as resulting from the superposition of relaxation processes in a completely amorphous sample of a polymer and relaxation processes occurring in a completely crystalline sample of the same polymer (17, 18, 4). An analogous assumption made by Chujo is well confirmed by NMR experiments carried out on crystalline polymers (see Chapter 6). Thus, the density of the retardation-time spectrum of a crystalline polymer, $L(\tau)$, may be expressed as follows:

$$L(\tau) = \kappa L_1(\tau) + (1 - \kappa) L_2(\tau) \quad (7.64)$$

where the subscript 1 refers to the completely crystalline sample and the subscript 2 to the completely amorphous sample of the same polymer.

Substituting Eq. (7.64) into Eq. (7.63) and assuming that $1/E_q$ depends on κ in the same way as does $L(\tau)$, we obtain:

$$J' = \kappa \left(\frac{1}{E_{1q}} + \int_0^{\infty} \frac{L_1(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + (1 - \kappa) \left(\frac{1}{E_{2q}} + \int_0^{\infty} \frac{L_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) \quad (7.65)$$

$$J'' = \kappa \int_0^{\infty} \frac{\omega \tau L_1(\tau) d\tau}{1 + \omega^2 \tau^2} + (1 - \kappa) \int_0^{\infty} \frac{\omega \tau L_2(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (7.66)$$

Since $J^* = 1/E^*$, it is clear that formulas (7.65) and (7.66) describe the dependence of the components of the complex modulus on the degree of crystallinity.

In the most frequently encountered case, where $\tan^2 \delta \ll 1$, $J' \approx \approx 1/E'$ and formula (7.65) assumes the following form:

$$\frac{1}{E'} = \kappa \left(\frac{1}{E_{1q}} + \int_0^{\infty} \frac{L_1(\tau) d\tau}{1 + \omega^2 \tau^2} \right) + (1 - \kappa) \left(\frac{1}{E_{2q}} + \int_0^{\infty} \frac{L_2(\tau) d\tau}{1 + \omega^2 \tau^2} \right) \quad (7.67)$$

Inspection of formulas (7.65) through (7.67) shows that two types of dependence of J' , E' , E'' , J'' and $\tan \delta$ on the degree of crystallinity are possible. Let us consider the case where the following inequality is valid:

$$\frac{1}{E_{1q}} + \int_0^{\infty} \frac{L_1(\tau) d\tau}{1 + \omega^2 \tau^2} < \frac{1}{E_{2q}} + \int_0^{\infty} \frac{L_2(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (7.68)$$

The inequality (7.68) will hold only when the storage compliance of the amorphous sample is substantially higher than that of the completely crystalline polymer. Obviously, this condition will be valid at temperatures higher than the glass-transition temperature of the amorphous regions. In this case, the major contribution to the quantities J' and $1/E'$ will come from the second terms on the right-hand side of formulas (7.65) and (7.67), and E' will increase with increasing crystallinity, while J'' will diminish. This relationship between E' and κ is encountered most often and is considered to be normal.

A comparison of expressions (7.64) through (7.68) shows that the sound velocity in this case will also increase with rising degree of crystallinity. If the following condition is satisfied along with relation (7.68)

$$\int_0^{\infty} \frac{L_1(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} < \int_0^{\infty} \frac{L_2(\tau) \omega \tau d\tau}{1 + \omega^2 \tau^2} \quad (7.69)$$

then the loss compliance J'' will be mainly determined by the second term on the right-hand side of formula (7.66). As a result, J'' will decrease with increasing crystallinity. Thus, a decrease in the loss compliance brought about by an increase in the degree of crystallinity of the polymer must accompany the normal dependence of the dynamic viscoelastic functions on the degree of crystallinity. Since $\tan \delta = J''/J'$, it evidently follows that the relationship between $\tan \delta$ and κ depends on which of the two functions (J' or J'') is more strongly dependent on κ . Both these parameters (J' and J'') decrease with rising κ provided that the conditions stipulated by (7.68) and (7.69) are fulfilled. However, at temperatures higher than the glass-transition temperature of the amorphous layer the loss compliance J'' depends on κ more strongly than does J' . Therefore, in this particular case, $\tan \delta$ must diminish with increasing degree of crystallinity.

Since $E'' = E' \tan \delta$, then it is obvious that when E' increases and $\tan \delta$ decreases with increasing crystallinity, there is possible a case where E'' will rise with increasing crystallinity. Such a dependence of E'' on κ may be expected to be most probable when the E'' peak corresponding to the unfreezing of segmental motion is located at a temperature which exceeds the glass-transition temperature by several tens of degrees. Thus, the different character of the dependence of E'' and J'' on the degree of crystallinity found by Gray and McCrum (16) for polytrifluorochloroethylene corresponds to the "normal" dependence of the dynamic viscoelastic functions on crystallinity.

The above-described dependence of the parameters E' , E'' , J' , J'' and c on κ can be observed not only at temperatures higher than the glass-transition temperature of the amorphous layer but also at $T < T_g$. Of decisive importance here is the fulfillment of the relations (7.68) and (7.69), which will hold if the intensity of relaxation processes in the amorphous sample substantially exceeds the intensity of relaxation processes taking place in the completely crystalline sample of the same polymer. Naturally, this condition is satisfied most frequently.

In cases where a crystalline polymer is at temperatures lower than the glass-transition temperature of the amorphous layer, the most intensive relaxation processes that make the major contribution to the relaxation spectrum of the amorphous sample may be found to be frozen, and the dynamic elastic modulus of the fully amorphous polymer may become sufficiently large (of the order of 10^3 to 10^4 MPa), and the storage compliance may accordingly become small. More often than not this is associated with the fairly effective intermolecular interaction of the kinetic units of neighbouring macromolecules, which are in the glassy state.

At the same time one can visualize such a completely crystalline polymer in which sufficiently intensive relaxation processes can occur at the same temperatures. One of the factors responsible for this may be a large number of defects in polymer crystals and the specificity of the packing of polymeric chains in them. Thus, below the glass temperature of the amorphous layer a case is possible where

$$\frac{1}{E_{1q}} + \int_0^{\infty} \frac{L_1(\tau) d\tau}{1 + \omega^2 \tau^2} > \frac{1}{E_{2q}} + \int_0^{\infty} \frac{L_2(\tau) d\tau}{1 + \omega^2 \tau^2} \quad (7.70)$$

The inequality (7.70) signifies that the principal role in formulas (7.65) and (7.67) is now played by the first term on the right-hand side and, hence, as κ increases the value of J' will increase and the dynamic elastic modulus E' decrease. Such an "anomalous" dependence of E' on κ , when the storage modulus and the sound velocity decrease with increasing degree of crystallinity has actually been observed (4) in such polymers as polytrifluorochloroethylene, polyethylene, and polyethylene terephthalate. At the same time, in all these polymers at a temperature higher than the glass temperature of the amorphous layer displays the usual dependence of the storage modulus and the sound velocity on κ , i.e., these parameters mount with rising degree of crystallinity.

The "anomalous" dependence of E' and c on crystallinity may also be treated in the following manner. It may be presumed that this dependence of E' and c on κ results from the competition of two phenomena. On the one hand, when the degree of crystallinity rises the total crystalline content in the polymer increases and the chain arrangement inside the crystallites become somewhat more ordered. This process must lead to an increase in the storage modulus and the sound velocity. On the other hand, as the degree of crystallinity increases the density of the amorphous layer is diminished and the intermolecular interaction becomes weaker. This effect will bring about a decrease in E' . This effect must be especially strongly pronounced when the intermolecular interaction in the amorphous layer is sufficiently strong, i.e., in the glassy state. The "anomalous" dependence of E' and c on κ is observed only in those cases where the second process is predominating. Note that the explanation given above is to a certain extent equivalent to the assumption that for such crystalline polymers, which exhibit the "anomalous" dependence of E' and c on κ , the Hosemann-Bonart model is valid.

7.5.2. Network Polymers

The most important characteristic of network polymers is the degree of cross-linking. The kinetic theory of viscoelasticity (see Chapter 3) allows one to establish the relationship between the

equilibrium modulus E_0 and the degree of cross-linking ν :

$$E_0 = \frac{3\rho RT}{M_c} = 3\nu RT \quad (7.71)$$

Formula (7.71) holds only for ideal network structures. For non-ideal networks the following expression is sometimes used:

$$E_0 = 3\Phi\nu RT \quad (7.72)$$

where Φ is a coefficient which takes account of the non-ideality of the space network (the front-factor); the magnitude of ν may depend on the concentration of the cross-linking agent and the functionality of the network junction.

The applicability of formulas (7.71) and (7.72) for the determination of the degree of cross-linking has been repeatedly tested through a comparison of the values of ν calculated from formulas (7.71) and (7.72) with those found by chemical methods or calculated from the composition of the reaction mixture with account taken of the extent of conversion of reactive groups. It has been found that if the equilibrium modulus E_0 is determined in the region of the rubbery plateau, the values of ν found from formulas (7.71) and (7.72) are in good agreement with the corresponding values obtained by other methods (4) even for such polymers as cured epoxide resins, which possess a sufficiently dense network. At present, it is evidently impossible to estimate strictly the limits of applicability of relations (7.71) and (7.72) for dense polymer networks. Nonetheless, one may assert that for all organic polymers the equilibrium modulus measured in the rubbery plateau region increases with network density. Such a dependence of the elastic modulus on the degree of cross-linking is encountered most frequently and is considered normal.

In order to establish the relationship between the acoustical properties of network polymers and the degree of cross-linking, let us employ relations of the types (7.34a) and (7.41). Then, in the case of a continuous relaxation-time spectrum the expression for Young's modulus can be written (4) in the form:

$$E' = E_0 + \int_0^{\infty} \frac{H(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (7.73)$$

Suppose that the density of the relaxation spectrum is expressed by the following relation:

$$H(\tau) = \varphi H_1(\tau) + (1 - \varphi) H_2(\tau) \quad (7.74)$$

where $H_1(\tau)$ is the density of the relaxation spectrum in a polymer with a maximum possible degree of cross-linking; $H_2(\tau)$ is the density of the relaxation spectrum in a polymer of the same chemical

structure but with no chemical cross-links; $\varphi = v/v_m$ (v_m is the maximum possible value of v).

Substituting expression (7.74) into (7.73), we get:

$$E' = E_0 + \varphi \int_0^{\infty} \frac{H_1(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau + (1 - \varphi) \int_0^{\infty} \frac{H_2(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (7.75)$$

Formula (7.75) allows one to explain, at least qualitatively, the dependence of E' on the degree of cross-linking at any temperatures and frequencies. Analogous expressions can also be obtained for the sound velocity.

It is evident that in the region of the rubbery plateau, when the condition $\omega\tau_j \ll 1$ is fulfilled for all $\omega\tau_j$, the second and third terms on the right-hand side of formula (7.75) may be neglected:

$$E' \approx E_0 = 3\nu RT$$

In this case, on the basis of acoustic measurements and relations (7.71) or (7.72) one can estimate the network density. Obviously, in the plateau region the storage modulus and the sound velocity will increase with increasing degree of cross-linking. Since in the region of the rubbery plateau $E' \approx E_0 = 1$ to 10 MPa, and in the glassy state $E' \approx 10^2$ to 10^3 MPa, it is evident that in the latter case the quantity E_0 in formula (7.75) can be neglected, and the major contribution to E will be introduced by the second and third terms on the right-hand side of expression (7.75). Here two cases are possible.

If we have

$$\int_0^{\infty} \frac{H_1(\tau) \omega^2 \tau^2 d\tau}{1 + \omega^2 \tau^2} > \int_0^{\infty} \frac{H_2(\tau) \omega^2 \tau^2 d\tau}{1 + \omega^2 \tau^2} \quad (7.76)$$

then the character of the dependence of E' on φ will be largely influenced by the second term on the right-hand side of expression (7.75) and the storage modulus will increase with increasing network density. Thus, the normal dependence of E' on φ for which E' is proportional to φ can be observed not only in the region of the rubbery plateau. In this case, however, the dependence of E' on φ is not unique. It is determined by the relationship between the spectra $H_1(\tau)$ and $H_2(\tau)$ and may vary, depending on the frequency and temperature.

A case is possible where the following condition is fulfilled:

$$\int_0^{\infty} \frac{H_1(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau < \int_0^{\infty} \frac{H_2(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\tau \quad (7.77)$$

Then, the major contribution to E' will come from the third term on the right-hand side of (7.75) and the storage modulus will decrease with increasing network density. Hence, formula (7.75) allows one to account for the "anomalous" dependence of the storage modulus on the degree of cross-linking. Such a dependence can be observed in the glassy state or in the region of transition from the glassy to the rubbery state.

The anomalous dependence of E' on ϕ at which E' falls off with rising network density is evidently intimately connected with a certain order in the chain arrangement in amorphous polymers below T_g . Imagine a linear amorphous polymer with reactive groups being in the glassy state. It is natural that the presence of "anticrystalline" clusters in such a polymer is possible, i.e., the presence of regions with a somewhat more ordered chain arrangement. The presence of such regions is perhaps the factor responsible for the high values (10^2 to 10^3 MPa) of the storage modulus of linear amorphous polymers below T_g .

If we introduce a certain amount of cross-linking agent and initiator into the melt of such a polymer, a network structure will be formed. Upon transition to the glassy state the chemical cross-links will hinder the formation of clusters, thereby reducing the intermolecular interaction between neighbouring chains. This in its turn will lead to a decrease in the storage modulus. The decrease in the storage modulus below T_g with increasing network density is probably explained by the fact that an increase in the number of chemical cross-links impedes the reduction of the distance between the kinetic units of neighbouring chains with decreasing temperature of the polymer, thereby reducing the effectiveness of the intermolecular interaction. In the rubbery state, where the kinetic units of neighbouring chains are highly mobile, the cross-links prevent the neighbouring chains from moving too far from one another, thereby increasing the intermolecular interaction, with the result that the storage modulus and sound velocity increase with increasing degree of cross-linking.

The anomalous dependence of E' on ν has actually been detected in cured epoxide resins and in copolymers of unsaturated polyesters and styrene (4).

7.5.3. Amorphous Polymers

It has been shown in the previous sections that the parameters characterizing the acoustic properties of polymeric materials depend, to a considerable extent, on their structure. This is especially important to the investigation of amorphous polymers, for which the "direct" structural methods do not provide, as a rule, sufficient information. The information on the supermolecular organization

of amorphous polymers obtained by means of acoustic investigations is usually scarce. This is accounted for, in particular, by the fact that acoustic measurements are carried out over a relatively narrow temperature range. Another factor that does not allow one to obtain information concerning the structure of polymers is the difference between the methods of acoustic measurements which complicates the comparison of experimental data. In this connection, attempts have been undertaken (19) to investigate the acoustical properties of some of the widely used amorphous polymers over a wide temperature range by the method of free torsional vibrations. The materials used for these investigations were atactic polystyrene, polyvinyl chloride, polymethyl methacrylate, polycarbonate, polysulphone.

Since the measurements covered a sufficiently wide range of temperatures, including the region of the rubbery plateau, it was possible to calculate the entanglement network parameters in amorphous polymers on the basis of the results obtained and by using the known dynamic shear modulus in the plateau region (where the modulus reaches an equilibrium value). According to the kinetic theory of rubberlike elasticity, the main characteristic of the network is the parameter M_c , which is defined as the average molecular mass of the chain portion between two neighbouring network entanglements. It is thought that another characteristic, which is of no less importance, is $n = M_c/M_0$ (where M_0 is the molecular mass of the repeating unit), which is the number of repeating units between two neighbouring entanglements and which determines, to a certain extent, the stiffness of the entanglement network. It is obvious that the greater the chain stiffness of the polymer, the lower is the parameter n . For example, the most rigid-chain polymer among the polymers studied, polysulphone, has $n = 2.4$; for polycarbonate $n = 3.7$; for polyvinyl chloride $n = 15$; for polystyrene $n = 33$; and for polymethyl methacrylate $n = 52$. It can naturally be expected that the larger the number of repeating units contained in the chain portion between two neighbouring entanglements, the higher the probability that upon transition from the rubbery to the glassy state there will be formed chain folds in an amorphous polymer.

It has been shown (9, 19) that the acoustic properties of amorphous polymers agree well with the concepts of anticrystalline clusters (4) in amorphous polymers (see Chapter 2). In the region of the well-developed rubbery state, in which an intensive segmental motion of the micro-Brownian type takes place, the clusters are destroyed or become fluctuational in character with a very short lifetime as a result of the thermal motion of the polymeric chains. The "memory" of the clusters is, however, retained in the rubbery state too. The material carrier of this "memory" is the entanglement network,

which is characterized by two constant parameters: the molecular mass of the chain portion between two neighbouring entanglements, M_c , and the number of repeating units contained in this fragment of the polymeric chain. The presence of an entanglement network is the factor responsible for the reproduction, in general features, of the previous supermolecular organization when the polymer passes to the glassy state.

The available experimental data (4, 9, 19) apparently confirm the cluster model of the supermolecular organization of amorphous polymers. A typical example is the temperature dependence of the sound velocity in the main relaxation region of amorphous polymers (9, 19). Many of the amorphous polymers studied display typically two temperature transitions in the glassy region which are recognized by a change in the temperature coefficient of the sound velocity $|\Delta c_t/\Delta T|$ (4, 9, 19). On the basis of the cluster model it may be supposed that the low-temperature transition T_2 in the glassy region which is usually more weakly pronounced is associated with the "unfreezing" of the segmental motion in the disordered regions of amorphous polymers. The high-temperature transition $T_1 = T_g$ in the glassy region which is always more distinctly pronounced and is characterized by the strongest change in the temperature coefficient of the sound velocity is apparently associated with the unfreezing of segmental motion inside the more ordered regions—inside the anticrystalline clusters.

It is interesting that the temperature interval ΔT_{1-2} between the points of the high-temperature T_1 and the low-temperature T_2 transition which are located in the main relaxation region depends strongly on the parameters that characterize the entanglement network. These transitions are closest to one another on the temperature scale in polysulphone ($\Delta T_{1-2} = 8^\circ\text{C}$), which has characteristically the lowest value of the parameter n . The highest value ($\Delta T_{1-2} = 37^\circ\text{C}$) is shown by polymethyl methacrylate, for which the value of n is the largest. It is natural to presume that the value of ΔT_{1-2} depends on the supermolecular organization of polymeric chains, the latter being in turn determined by the stiffness of the entanglement network, i.e., in the final run by the chemical structure of the polymer. Indeed, if one proceeds from the concepts described above, the clusters must be expected to be formed for such rigid-chain polymers as polysulphone ($n = 2.4$) and polycarbonate ($n = 3.7$) by portions of straightened-out chains and no chain folds to be present in the clusters. Thus, the difference in chain morphology and, hence, in activation energy of relaxation processes associated with the unfreezing of segmental motion between the disordered matrix and the ordered clusters is not large. This is what leads to the close disposition of the two temperature transitions in the glassy state. This is also responsible for the fact that the width of the transition zone,

i.e., the temperature interval between the glass temperature T_1 and the temperature at which the rubbery plateau starts, is rather narrow for polysulphone and polycarbonate. It is equal to 11°C for polysulphone and 19°C for polycarbonate. The fact that the transition from the glassy to the rubbery state in these polymers occurs within a very narrow temperature range, which is narrower than the melting region of some crystalline polymers, is an indication of the high degree of cooperativity of the glass transition process in polysulphone and polycarbonate. This cooperativity is in turn due to the peculiar morphology of polymeric chains, which evidently form very few (or do not form at all) folds.

It may be expected that when anticrystalline clusters are formed by straightened-out lengths of the chains that do not form folds, the segmental motion will become unfrozen within a relatively narrow temperature range and that the dynamic measurements of mechanical parameters will involve an intensive dissipation of the energy of sound vibration. The change from the glassy to the rubbery state in polymers with anticrystalline clusters formed by polymeric chain folds must evidently occur over a broader temperature range, as a result of which the height of the loss peak will be reduced and the transition zone widened. Thus, polymers with a small value of n must display a higher loss peak than those with a large n . This is consistent with the available experimental data (19). For example, polysulphone and polycarbonate have the highest loss peaks in the region of transition from the glass to the rubbery state: for them $\tan \delta_{\max} \approx 7.5$, while for polymers with large values of n the loss peaks in the glassy region are smaller: for polystyrene ($n = 33$) $\tan \delta_{\max} \approx 1.2$, and for polymethyl methacrylate ($n = 52$) $\tan \delta_{\max} \approx 0.66$.

An interesting regularity is observed: the narrower the temperature range corresponding to the transition from the glassy to the rubbery state, the higher the loss peak associated with this relaxation process. Thus, the nature of the entanglement network (i.e., the values of the quantities M_e and n) specifies, as it were, the chain morphology in an amorphous polymer and thereby determines the degree of cooperativity of segmental motion upon transition from the glassy to the rubbery state.

The entanglement network density has a substantial effect on the acoustical properties of amorphous polymers in the region of the rubbery plateau. It has been found that, according to the stiffness of the entanglement network, all the polymers studied can be classified into two groups, whose G_0 values differ by about five times. For polymers with small n values (polysulphone, polycarbonate, polyvinyl chloride) the modulus G_0 is equal to about 5 MPa in the region of the rubbery plateau, while for those with large n values (polystyrene, polymethyl methacrylate) $G_0 \approx 1$ MPa. The

appreciable difference between the values of the shear modulus of polymers in the region of the rubbery plateau leads one to believe that the probability of the conformations corresponding to extended chains being formed is greater for such polymers as polysulphone, polycarbonate and polyvinyl chloride in the glassy state. At the same time, polymers with a substantially smaller modulus in the rubbery plateau region must form, in the glassy state, ordered regions consisting of chain folds.

If the above supposition is valid, one can expect that in the glassy state more rigid and denser entanglement networks will prevent the polymer chains from being tightly packed, and therefore the storage modulus of such polymers in the glassy state will be lower than for polymers with a sparser entanglement network. It is precisely this regularity that has been detected in investigations of the viscoelastic properties of amorphous polymers at low temperatures (20). It has been established that the shear modulus $G' = 3.2 \times 10^3$ MPa for polymethyl methacrylate ($n = 52$) at 4.2 K, and for polycarbonate ($n = 3.7$) at the same temperature $G' = 2.2 \times 10^3$ MPa.

The specific features of the supermolecular organization of amorphous polymers, which may be characterized by the parameter n , as has been shown above, manifest themselves distinctly in the temperature dependence of the sound velocity at $T > T_g$. It has been found that above the glass-transition temperature the value of the temperature coefficient of the sound velocity $|\Delta c_t/\Delta T|$ is approximately inversely proportional to the parameter n (19). The value of $|\Delta c_t/\Delta T|$ measured above the temperature of any temperature transition may apparently serve as a sort of indicator of the cooperativity of the relaxation process. Admittedly, the higher the value of $|\Delta c_t/\Delta T|$, the greater is the degree of cooperativity of the molecular motion responsible for this relaxation process.

From what has been said above it follows that the supermolecular organization of an amorphous polymer and its acoustic properties are determined by its chemical structure. We may even assert that each macromolecule of a given polymer contains information on the nature of its supermolecular organization, the most important temperature transitions and physical properties.

At present, only first attempts are being made to use the results of acoustic measurements in order to decipher at least part of the information stored in polymeric chains.

References

1. Ferry, J. D., *Viscoelastic Properties of Polymers*, John Wiley and Sons, Inc., New York, 2nd ed., 1970.
2. Bland, D. R., *Theory of Linear Viscoelasticity*, Pergamon, Oxford, 1960.

3. Mikhailov, I. G., V. A. Soloviev, and Yu. P. Syrnikov, *Foundations of Molecular Acoustics*, Nauka, Moscow, 1964 (in Russian).
4. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers, Moscow, 1975.
5. Landau, L. D. and E. M. Lifshitz, *Theory of Elasticity*, 2nd ed., Pergamon Press, New York, 1970.
6. Waterman, H. A., *Koll.-Z.*, **196**, 1, 18 (1964).
7. Crissman, J. M. and E. Passaglia, in: *Transitions and Relaxations in Polymers*, edited by R. Boyer, New Jersey, 1966.
8. Hoffmann, J. D., G. Williams, and E. Passaglia, in: *Transitions and Relaxations in Polymers*, edited by R. Boyer, New Jersey, 1966.
9. Perepechko, I. I., and O. V. Startsev, *Vysokomol. Soedin.*, **B**, **15**, 5, 324 (1973).
10. Bartenev, G. M. and I. Lukyanov, *Zhurn. Fiz. Khim.*, **29**, 8, 1486 (1955).
11. Shishkin, N. I., *Zhurn. Fiz. Khim.*, **26**, 7, 1461 (1956).
12. Bueche, F., *J. Chem. Phys.*, **24**, 2, 418 (1956).
13. Macedo, P. B. and T. A. Litovitz, *J. Chem. Phys.*, **42**, 1, 245 (1965).
14. Sauer, J. A. and R. G. Saba, *J. Macromol. Sci.*, **A**, **3**, 7, 1217 (1969).
15. Bartenev, G. M. and Yu. V. Zelenev, *Mekhanika Polimerov*, **1**, 30 (1969).
16. Gray, R. W. and N. G. McCrum, *J. Polymer Sci.*, **B**, **4**, 9, 639 (1966).
17. Perepechko, I. I., *Akust. Zhurn.*, **13**, 1, 143 (1967).
18. Perepechko, I. I., *Mekhanika Polimerov*, **3**, 437 (1969).
19. Perepechko, I. I. and O. V. Startsev, *Akust. Zhurn.*, **22**, 5, 749 (1976).
20. Perepechko, I. I., *Low-Temperature Properties of Polymers*, Mir Publishers, Moscow and Pergamon Press, Oxford, 1980.

Chapter 8

The Strength of Polymers

8.1. Basic Concepts of Strength and Durability

One of the most important physical characteristics of polymers that determine their performance is the strength. Mechanical strength is taken to mean the ability of solids to withstand fracture under the applied forces. For the strength to be estimated quantitatively, several characteristics are used. One of the most extensively employed strength characteristics is the stress σ_f at which the material is fractured. Usually, the fracture stress σ_f is measured with the aid of tensile machines as the limiting (maximum) stress at which the specimen undergoes fracture. In view of this, the quantity σ_f is often called the ultimate strength. The conventionality of this definition of σ_f will be shown later.

The fracture stress σ_f depends on the properties of the material itself and also on the temperature and rate of strain. It is for this reason that a comparison of the values of σ_f of various polymers has meaning only when they are measured at the same temperature and at the same rate of strain.

It has long been believed that fracture can occur only in those cases when the stress in the specimen exceeds a certain critical value. It has, however, been found (1-6) that many materials can be fractured when the applied stress is considerably less than σ_f measured by a standard method. The decisive factor in this case is the time during which the polymer specimen is loaded. If this time is sufficiently long, fracture can in a number of cases occur at stresses much smaller than σ_f . The time from the moment the load is applied to the specimen up to the break is called the durability. The durability τ is an important strength characteristic. Usually, in an experimental investigation of the durability the stress is maintained constant ($\sigma = \text{const}$). If this condition is not fulfilled, the time dependence of strength at a constant load characterizes the static fatigue. The time dependence of strength for dynamic loading (the sample is most often subjected to a periodic stress) characterizes the dynamic fatigue.

The behaviour of the material at the moment of fracture is described by the amount of the maximum relative deformation ϵ_f at break (the fracture strain). The fracture strain ϵ_f depends on the type of strain, the rate of strain, temperature and, to a considerable extent,

on the chemical structure and physical properties of the material. With a brittle fracture the relative deformation ε_f is hundredths of a percent. When the polymer in the rubbery state undergoes a fracture, the relative deformation may reach several hundreds of a percent.

The strength of a solid can be calculated theoretically. To this end, it is necessary to know the structure of the crystal and the nature of the forces acting between the particles that reside in the crystal lattice points. As a matter of fact, this task can be solved only in the case of an ideal single crystal. An accurate calculation of strength is a very difficult undertaking; at present only the strength of single crystals of rock salt (NaCl) formed by the ions Na^+ and Cl^- has been calculated correctly. The strength of NaCl single crystals in uniform extension has been calculated by Born (7) and in uniaxial extension by Zwicky (8). From the calculations carried out by Zwicky it follows that the strength σ_f of the single crystals of rock salt must be 2×10^3 MPa, which is 400 times greater than the experimentally found value (5.31 MPa).

It was formerly believed (8) that the cause of such a large difference between the theoretical strength and the actual strength is accounted for by the fact that theoretical calculations do not take account of thermal motion. As a matter of fact, the theoretical calculations carried out by Zwicky must, strictly speaking, be valid only at $T = 0$ K. In these computations, use was made of the Mee interaction potential:

$$U = -\frac{A_m}{x^m} + \frac{B_n}{x^n} \quad (8.1)$$

where U is the potential interaction energy per one particle (an ion); x is the distance between two neighbouring particles in the extension direction; A_m and B_n are constants; m and n are the parameters which depend on the nature of the interaction between the particles (for NaCl crystals $m = 1$ and $n = 9$).

It is obvious that the quasi-elastic force per particle is given by:

$$F = -\frac{\partial U}{\partial x} \quad (8.2)$$

The external force acting on one particle is equal to dU/dx . Analysis of expressions (8.2) and (8.1) shows that as the distance between neighbouring particles increases the quasi-elastic force passes through a maximum and then vanishes. It is clear that the crystal will fracture on extension only in those cases when the external force that causes the extension will be greater than the maximum value F_m of the quasi-elastic force. If the external force is less than F_m , no fracture is possible and only an elongation will take place. Obviously, this model does not take into account the thermal motion of

the particles that make up the crystal lattice and the presence of defects in this lattice.

The methods of calculation employed by Born and Zwicky are inapplicable to amorphous polymers. Orowan (9) suggested a semi-empirical method of calculating theoretical strength. He used an approximate equation for the quasi-elastic force F acting on a particle:

$$F = F_m \sin \left[\frac{\pi}{a_0} (x - x_0) \right] \quad (8.3)$$

where F_m is the maximum value of the quasi-elastic force; a_0 is the doubled distance from the equilibrium position of the particle to the position in which the quasi-elastic force reaches a maximum value; x is the interparticle distance; x_0 is the equilibrium interparticle distance (at $x = x_0$, $F = 0$).

When two unit areas located at right angles to the direction of the tensile force move slowly apart, the quasi-elastic force will be equal to the external tensile force. In this case, the stress is given by the following formula:

$$\sigma = NF \quad (8.4)$$

where N is the number of particles per unit area.

Using expressions (8.4) and (8.3), we can write:

$$\sigma = \sigma_m \sin \left[\frac{\pi}{a_0} (x - x_0) \right] \quad (8.5)$$

where $\sigma_m = NF_m$. The quantity σ_m was treated by Orowan as the theoretical strength. According to Orowan, the stress σ_m is connected with the free surface energy of a solid, α_s , by the following relation:

$$\sigma_m 2a_0 / \pi = 2\alpha_s \quad (8.6)$$

The constant a_0 can be determined by using Hooke's law:

$$a_0 = \sigma_m \cdot \pi x_0 / E \quad (8.7)$$

where E is Young's modulus. Substituting expression (8.7) into formula (8.6), we obtain the well-known Orowan formula for calculation of theoretical strength:

$$\sigma_m = \sqrt{\alpha_s E / x_0} \quad (8.8)$$

Since the free surface energy is, as a rule, unknown for polymers, crude estimations of the strength are sometimes made through the use of formula (8.7), taking into account that the maximum value of the quasi-elastic force is realized when the bonds are stretched by 10-20 per cent. In this case, $a_0/2 = (0.1 \text{ to } 0.2) \cdot x_0 \approx 0.15x_0$. Substituting this value into formula (8.7), we get:

$$\sigma_m \approx 0.1E \quad (8.9)$$

Kobeko (10), who used a different method of calculation and the Morse potential, showed that formula (8.9) is valid for any type of bond. The estimating formula (8.9) is often used to calculate theoretical strength.

We have already said above that the experimentally measured strength is considerably less (by 2-3 orders of magnitude) than the theoretical strength. The first attempt to account for this discrepancy was made by Griffith (11) who developed the first physical theory of strength. Griffith assumed that in a real solid body (especially in its surface layer) there are a large number of flaws in the form of microcracks of various sizes and orientations. When the sample is subjected to an external load, around the microcracks there develops a concentration of stress, which considerably exceeds the mean stress within the specimen. According to Griffith, the fracture of the material occurs only in those cases when the large concentrated stresses σ_0 at the tip of the most dangerous crack prove to be equal to or greater than the theoretical strength σ_m . At $\sigma_0 \geq \sigma_m$ the most critical crack begins to grow catastrophically (at a velocity close to the sound velocity) and the specimen is broken into two parts. At $\sigma_0 < \sigma_m$ the crack does not grow.

In those cases when the concentrated stress σ_0 turns out to be equal to σ_m and the microcrack starts growing, the external stress applied to the specimen, σ_c (the critical stress), will naturally be considerably less than the theoretical stress σ_m . Evidently, the critical stress, in contrast to σ_m , is not a constant for the material and varies from sample to sample, since it greatly depends on the shape, size and orientation of microcracks. These parameters also determine the stress concentration factor at the crack tip, $\beta = \sigma_0/\sigma$.

The Griffith theory rests on the law of conservation of energy as applied to brittle fracture. Griffith assumed that the crack propagates only when the change in the elastic energy in the specimen brought about by the unloading of the specimen in the vicinity of the propagating crack is equal to (or greater than) the change in the surface energy of the freshly created interfaces. Equating the change in the elastic energy ΔW to the change in the surface energy, Griffith derived the following expression for the critical stress:

$$\sigma_c = \frac{2}{\sqrt{\pi}} \sqrt{\frac{\alpha_s E}{\mu c}} \quad (8.10)$$

where μ is Poisson's ratio; c is the internal crack length (it is assumed that the crack has an elliptical form and that the tensile force is directed perpendicular to the major semi-axis of the ellipse).

Thus, the Griffith theory clearly indicates that the technical strength of the material must be lower than theoretical strength because σ_c depends on the natural flaws which always exist in real solids.

The Griffith theory has a number of shortcomings, of which two are the most important. It does not take into account the thermal motion of atoms and therefore the athermal mechanism of fracture is assumed. The Griffith theory cannot account for the time dependence of strength which is, as a rule, observed experimentally. Because of these shortcomings, the Griffith theory may be regarded as being physically substantiated only at $T \rightarrow 0$ K.

A further shortcoming of the Griffith theory is that it does not take account of mechanical losses resulting from the brittle fracture of the material. Indeed, as has been said above, the basic premise in the Griffith theory is the equality of the change in the elastic energy dW to the increase in the surface energy $d\varepsilon$ when the crack is growing. This condition, however, can be fulfilled only in the state of equilibrium, when the rate of propagation of the crack tends to zero (which is equivalent to the condition $\partial W/\partial c = 0$). If the growth of the crack occurs at a finite velocity, part of the elastic energy is dissipated, being converted into heat. Obviously, the law of conservation of energy must be written in this case in the following form:

$$-dW = d\varepsilon + dQ' \quad (8.11)$$

where dQ' is the energy dissipated at fracture.

At $dQ' = 0$ (a case corresponding to the Griffith theory) the crack must not grow. The fracture of solids usually involves several kinds of energy losses. They include (1): losses associated with the dissipation of energy as a result of the attenuation of atomic vibrations after the bonds are ruptured; losses that arise as a result of the separation of crack walls and the unloading of the material near the crack; losses due to the viscous or plastic flow at stress concentration sites.

The Griffith theory is a phenomenological theory of strength. Numerous experimental findings have led to the development of a molecular theory of strength based on the study of the physical kinetics of the fracture process.

It has been established that solids (including polymers) can fracture at stresses $\sigma < \sigma_c$, i.e., when the stress concentration at the crack tip $\sigma_{sc} < \sigma'_{sc}$, where σ'_{sc} is the critical stress concentration (1). It has been said above that in this case there is observed the time dependence of strength caused by the fatigue of the material.

The fatigue of polymeric materials substantially depends on temperature. As the temperature is lowered down to very low temperatures the fatigue phenomenon disappears. In this connection, there has been developed the concept of two different fracture mechanisms. It is natural to assume that at low temperatures (when $T \rightarrow 0$ K) fracture occurs only under the action of the applied mechanical stress (the athermal mechanism), and at higher temperatures

it results from the action of mechanical stresses and thermal vibrations of atoms and molecules (the thermal mechanism of fracture). A systematic investigation of the time dependence of the strength of solids associated with the effect of the thermal fluctuations of atoms on the fracture process has been carried out by Zhurkov and his coworkers (2, 12-14). It has been found that the time dependence of strength in uniaxial extension (provided that $\sigma = \text{const}$) for various polymeric materials (oriented, as a rule) is described by the following formula:

$$\tau = Ae^{-\alpha\sigma} \quad (8.12)$$

where τ is the durability; σ is the specified tensile stress; α and A are constants which depend on the nature of the material and temperature.

Zhurkov and his coworkers have shown that the temperature dependence of durability is expressed by the following equation:

$$\tau = \tau_0 e^{(U_0 - \gamma\sigma)/kT} \quad (8.13)$$

where τ_0 is a constant which is close in value to the period of thermal oscillations of atoms (according to Zhurkov, $\tau_0 \approx 10^{-12}$ to 10^{-13} s for all polymers); U_0 is the energy of activation of the elementary act of fracture in the absence of external stress (the magnitude of U_0 is close to the energy of chemical bonds for polymers and to the sublimation energy for metals); k is Boltzmann's constant; T is the absolute temperature; σ is the stress applied to the specimen; γ is a coefficient which depends on the nature and structure of the material (a structure-sensitive parameter).

Taking the logarithms of Eq. (8.13), we obtain:

$$\log \tau = \log \tau_0 + \frac{1}{2.303k} \cdot \frac{1}{T} (U_0 - \gamma\sigma) \quad (8.14)$$

Analysis of Eq. (8.14) shows that the dependence of the logarithm of durability on the inverse temperature is expressed by a straight line, the slope of which depends on the parameters U_0 , γ and σ . From this it follows that for specimens of the same material which are subjected to different stresses σ , the dependence of $\log \tau$ on the inverse temperature must be in the form of a family of straight lines originating from the same pole (Fig. 8.1).

If we construct a plot of $\log \tau$ against σ for a single material tested at different temperatures, then, as follows from Eq. (8.14), a family of straight lines will be obtained, which also originate from a single pole; this pole must evidently correspond to the stress $\sigma = \sigma_c$. A typical dependence of $\log \tau$ on the stress σ is given in Fig. 8.2. From Eq. (8.14) it follows that the slope of the straight line expressing the dependence $\log \tau = f(\sigma)$ increases (in absolute value) with decreasing T . This inference is in good agreement with experimental

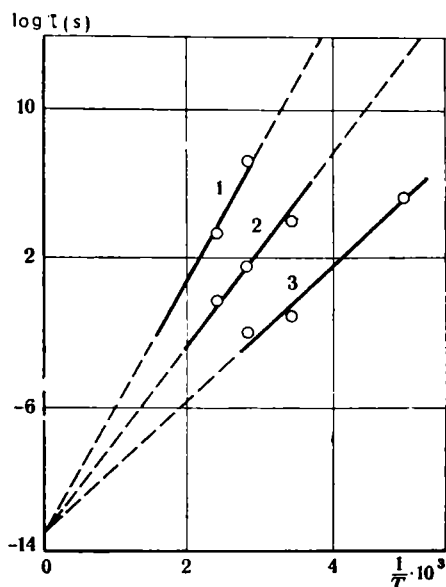


Fig. 8.1. Dependence of the logarithm of durability τ on inverse temperature for viscose fibre at various stresses: 1—200 MPa; 2—400 MPa; 3—600 MPa.

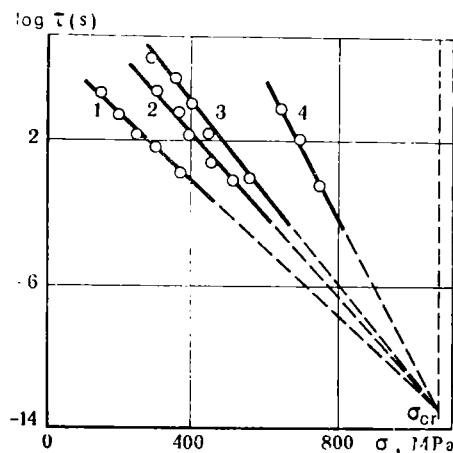


Fig. 8.2. Dependence of the logarithm of durability τ on the applied stress σ for viscose fibre at various temperatures: 1—150°C; 2—80°C; 3—20°C; 4—minus 75°C.

data (see, for example, Fig. 8.2). As the temperature is lowered the $\log \tau = f(\sigma)$ straight lines become increasingly steeper. At rather low temperatures (for plastics, at temperatures $T < -200^\circ\text{C}$) the graph of $\log \tau$ versus σ runs so steeply that this straight line becomes almost parallel to the y axis. This means that at low temperatures the breaking stress is independent of the loading time. Hence, at stresses $\sigma < \sigma_c$ no fracture practically occurs.

In this connection it becomes clear that at sufficiently low temperatures at which no time dependence of strength is observed, the critical strength σ_c (or, what is the same thing, the ultimate strength) is a definite and unambiguous characteristic of a solid. In those cases when the time dependence of strength is observed, the concept of the ultimate strength becomes indeterminate if the time during which the specimen is in the stressed state is not specified.

A comparison of Eq. (8.12) with Eq. (8.13) or (8.14) allows one to come to the conclusion that the constants A and α in Eq. (8.12) are given by the following relations: $A = \tau_0 \exp(U_0/kT)$ and $\alpha = \gamma/kT$.

The validity of Eqs. (8.12) and (8.13) has been tested on a large variety of polymeric materials, metals, glasses. At present, there are a large amount of experimental data which confirm the time dependence of strength predicted by these equations.

In limiting cases, however, Eq. (8.13) does not hold. Let us consider two cases: (1) if $\sigma = 0$ (the specimen is not loaded), then $\tau = \tau_0 \exp(U_0/kT)$; (2) the specimen is subjected to an external stress σ_c such that $U_0 - \gamma\sigma_c = 0$, in which case $\sigma_c = U_0/\gamma$ and the durability $\tau = \tau_0$, i.e., it turns out to be the same for any temperature.

In the two cases considered Eq. (8.13) is not fulfilled. Indeed, in the first case ($\sigma = 0$) it turns out that in the absence of a stress a solid can exist only for a limited period of time, which naturally is meaningless and does not agree with experiment. In the second case ($\sigma = \sigma_c = U_0/\gamma$) the durability at all temperatures must be equal to 10^{-12} s. The unreality of such a situation for samples having finite dimensions is obvious.

Thus, Eq. (8.13) is valid only over a certain definite range of stresses and loading times.

Inspection of Eq. (8.13) and numerous experimental data shows that the principal role in the fracture of solids (including polymers) is played not only by the externally applied stress but also by the thermal motion of atoms, the intensity of which increases with increasing temperature. The application of an external load leads to a decrease in the height of the effective potential barrier of the fracture process:

$$\Delta U = U_0 - \gamma\sigma \quad (8.15)$$

In this equation U_0 is the initial activation barrier, the magnitude of which is usually commensurable with the activation energy of the thermal degradation of polymers; $\gamma\sigma$ is in essence the part of work done by the external forces during the fracture of a solid. The remaining part of the work of rupture of chemical bonds is done by the energy of the thermal fluctuations of atoms.

8.2. The Mechanism of Polymer Fracture. The Thermofluctuational Theory

The present-day conceptions of the fracture mechanism in polymers and of the role of thermal fluctuations in this process have been worked out in the works of Aleksandrov (15), Zhurkov (2, 12-14), Bartenev (1) and by a number of other investigators. It has been found that the fracture of polymers is associated with the initiation and growth of microcracks. It is customarily believed that the fracture process consists of two stages. The first stage involves the initiation and growth of cracks; at the second stage the cracks are rapidly propagating and spread throughout the entire cross-section of the specimen, resulting in its fracture.

Zhurkov and his coworkers have established that the primary cracks in a polymer are initiated by thermal fluctuations. The thermal fluctuations bring about an increase in the kinetic energy of

individual atoms, which are vibrating about their equilibrium positions, this leading sometimes to the rupture of the chemical bonds in the main chain of the polymer. This happens in those cases when the kinetic energy of atoms exceeds the chemical bond energy. The rupture of chemical bonds is accompanied by the process of their re-formation. The stresses that result from the externally applied load reduce the activation energy of the process of breaking of chemical bonds, and the thermal fluctuations lead to their rupture. The thermofluctuational theory of strength proceeds from the assumption that the rupture of chemical bonds is caused by thermal fluctuations and that the stress lowers the probability of these bonds being re-formed, thereby making the fracture process proceed in a definite direction.

According to the thermofluctuational concept of strength (16), for a body to fail, i.e., to be broken into parts and become unsuitable for its intended use, all the interatomic bonds must be ruptured in any of its cross-section. It follows that the durability of a solid body is the time required for thermal fluctuations (with a sufficiently high energy) to get to most of the interatomic bonds in a given cross-section. During the time approximately equal to the durability τ the fluctuations reach almost all the atoms situated in a given cross-sectional area, bringing about the rupture of the interatomic bonds; this leads eventually to the failure of the specimen. Here it is presumed that the fluctuational energy exceeds the height of the effective potential barrier ΔU .

Let us consider one of the variants of the thermofluctuational theory of strength proposed by Bartenev (17). Suppose we have a material which undergoes a brittle fracture. This refers to polymers below the brittle temperature T_b and also in the range from T_b to T_g .

The most dangerous flaws in polymeric materials that fracture in a brittle fashion are microcracks and submicrocracks, which exist until an external stress is applied. Obviously, the growth of such microcracks which takes place at the first (slow) stage of the fracture process is exactly the factor that determines the durability of the material. Let us consider the rupture of an interatomic bond at the tip of a microcrack. For this rupture to be effected, it is necessary that a potential barrier of height U be surmounted (Fig. 8.3). We have already said that the rupture of the bonds between atoms may be accompanied by the process of their re-building. For the latter process to be accomplished, it is necessary to overcome the potential barrier U' , whose magnitude is lower than U ($U' < U$) if the polymer is not loaded. Figure 8.3 presents the dependence of the potential energy of atoms at the microcrack tip on the distance between them. The minimum of the potential energy situated on the left corresponds to the equilibrium position of the atoms far

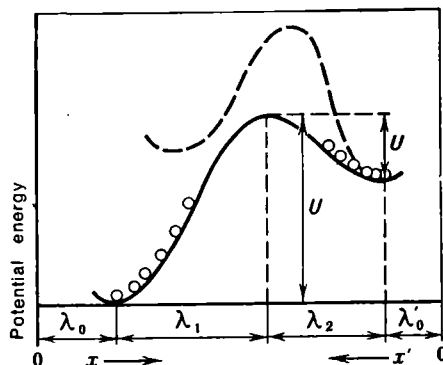


Fig. 8.3. Dependence of the potential energy on the internuclear distance. For explanations, see the text.

from the crack; the second minimum located on the right corresponds to the equilibrium position of the atoms, which are at the free surface of the specimen after their bonds are broken. The surface potential energy of a solid body referred to two atoms, the bond between which has been broken, is equal to the difference

$$U - U' = 2\alpha_s \lambda_0 \quad (8.16)$$

where α_s is the potential surface energy; λ_0 is the equilibrium distance between the particles.

From Fig. 8.3 it is seen that the crack must close up to its initial dimensions in the absence of externally applied loads, since the probability of finding atoms in the left (deeper) minimum is greater than that in the right one.

Evidently, with a large tensile stress the probability of the broken bonds being re-formed diminishes and the asymmetry of the potential energy changes sign (see the dashed line curve in Fig. 8.3). Now the probability that the atoms will have a potential energy corresponding to the right minimum in Fig. 8.3 is found to be higher than the probability of the atoms residing in the left minimum. This means that the bond rupture becomes more probable.

Suppose we have a polymer sample in the form of a thin strip. Let us consider the fracture process taking place on uniaxial extension of this specimen. Since the largest number of critical flaws arise in cutting out the specimen at its edges, the crack begins growing from the edge of the strip at right angles to the extension direction.

Under the action of the stress σ applied to the polymer specimen, a stress concentration develops at the tip of the edge crack, the length of which is l :

$$\sigma_{sc} = \beta \sigma' \quad (8.17)$$

where σ' is the stress in the unfractured cross-sectional area of the specimen; β is the stress concentration factor. Here it is presumed that the crack grows in a direction perpendicular to the direction

of extension. The crack length changes from l (the original length) to L (the width of the specimen).

The second stage of the fracture process (the critical fracture), according to Bartenev, occurs at the moment when the critical stress concentration σ'_{sc} is attained at the crack tip, which contributes to the rupture of the bonds and hinders their re-formation.

If the stress concentration at the crack tip is such that the potential-energy curve in Fig. 8.3 becomes symmetrical, it is called the safe local stress σ_{sc0} . If the stress concentration $\sigma_{sc} > \sigma_{sc0}$, the crack grows; if $\sigma_{sc} < \sigma_{sc0}$, the crack closes up. The stress applied to the specimen, σ_0 , under the action of which the safe stress concentration is developed at the crack tip is called the safe stress. The frequency of fluctuations that lead to the growth of the crack is given by:

$$v_1 = v_0 e^{-\frac{U - \omega \beta \sigma'}{kT}} \quad (8.18)$$

The frequency of fluctuations that lead to the closing-up of the crack is determined by the following expression:

$$v_2 = v_0 e^{-\frac{U' + \omega' \sigma'}{kT}} \quad (8.19)$$

In Eqs. (8.18) and (8.19), v_0 is the frequency of vibrations of a group of atoms which participate simultaneously in the breaking or re-formation of the bonds ($v_0 \approx 10^{12} \text{ s}^{-1}$ for polymers); ω and ω' are the volume elements in which the rupture or re-formation of the bonds occurs during thermal fluctuations. The parameter ω plays an important role in the thermofluctuational theory of strength and is called the fluctuational volume. The fluctuational volume $\omega = \lambda_1 \lambda \lambda_\pi$ and $\omega' = \lambda_2 \lambda \lambda_\pi$, where λ is the distance travelled by the front of the microcrack on each fluctuation (λ is close, in order of magnitude, to the interatomic distance); it is presumed that $\lambda \approx 3\lambda_0$, where λ_0 is the mean intermolecular distance in the polymer. The parameter λ_π is the elementary length of the crack perimeter which consists of one or more atoms simultaneously involved in the fluctuation ($\lambda_\pi \approx 2\lambda_0$). The parameters $\lambda_1 \approx \lambda_2 \approx \lambda_m$ are the distances between the corresponding minimum and maximum of the potential energy (see Fig. 8.3). Gubanov and Chevychelov (18, 19) have shown that the value of λ_m for organic polymers is about the same as the C—C bond length ($\lambda_m = 1.5 \text{ \AA}$). For example, in the case of polymethyl methacrylate $\lambda_0 \approx 5 \text{ \AA}$ and the fluctuational volume $\omega = 2.25 \times 10^{-19} \text{ mm}^3$. From the fluctuational theory it follows that the rate of growth of the crack is $v_1 = \lambda v_1$ and the rate at which it closes up is $v_2 = \lambda v_2$. It is obvious that the net rate of growth of the microcrack $v = v_1 - v_2$, where v_1 and v_2 are the fluctuational rates of growth and closing-up of the microcrack which

are defined by Eqs. (8.18) and (8.19). Hence, we obtain the following expression for v :

$$v = v_c \left[e^{-\frac{U - \omega\beta\sigma'}{kT}} - e^{-\frac{U' + \omega\beta\sigma'}{kT}} \right] \quad (8.20)$$

where $v_c = \lambda v_0$ is the critical rate of growth of the microcrack.

For polymers $v_c \approx 1500$ m/s, which is close, for example, to the limiting rate of fracture of polymethyl methacrylate (about 700 m/s) and to the sound velocity in this polymer (the velocity of longitudinal waves measured at a frequency of 200 Hz in polymethyl methacrylate is about 1800 m/s). The durability of the specimen on static loading ($\sigma = \text{const}$), when the stress is in the range from σ_0 to σ_c , is made up of the time to break at the first and second stages:

$$\tau = \int_0^{l_c} \frac{dl}{v} + \int_{l_c}^L \frac{dl}{v_c} \quad (8.21)$$

where l_c is the microcrack length corresponding to the onset of the second stage of the fracture process; L is the width of the specimen.

Integration of expression (8.21) with the use of Eq. (8.20) leads, within a limited range of σ values and with a number of simplifying assumptions made, to the following expression for the durability:

$$\tau = C e^{\frac{U - \gamma\sigma}{kT}} \quad (8.22)$$

where $\gamma = \beta\omega$ and the factor C is given by

$$C = \frac{LkT}{\lambda v_0 \omega \beta \sigma} \quad (8.23)$$

At first glance it seems strange that expression (8.22) coincides with the well-known Zhurkov formula (8.13). The difference, however, is not only that C depends on temperature ($\tau_0 = 10^{-12}$ s = const) but also in that $C = (10^{-5}$ to $10^{-6})$ s for polymers. It has been found (1, 17, 20) that from expression (8.22) one can obtain formula (8.13) if it is assumed that the activation energy U of the fracture process is linearly dependent on temperature:

$$U = U_0 - aT \quad (8.24)$$

where U_0 is the energy of activation at 0 K; a is a constant which depends on the type of bond and the structure of the material. In this case, expression (8.22) assumes the form

$$\tau = \tau_{01} e^{\frac{U_0 - \gamma\sigma}{kT}} \quad (8.25)$$

Here τ_{01} is no longer the period of vibration of atoms (as it follows from the Zhurkov concepts) but is defined by the following expres-

sion:

$$\tau_{01} = \frac{LnkTe^{-a/k}}{v_0\beta\omega\sigma} \quad (8.26)$$

where $n = 1/\lambda$ is the number of chains broken per unit crack length. For polymers, formulas (8.25) and (8.13) coincide provided that $\tau_0 = \tau_{01}$; $a = 113$ kJ/(mole·K); $ke^{-a/k} = 3.5 \times 10^{-29}$ kgf·cm/K.

It should be noted that formula (8.25) is in essence an interpolation formula, though it is applicable over a sufficiently wide range of durability (from 10^{-3} to 10^8 s). This formula holds only within the range of σ values between σ_0 (the safe stress) and σ_c (the critical stress). The thermofluctuational theory of strength (1, 17, 20) allows one to describe, at least qualitatively, the durability of polymers in limiting cases (when $\sigma \rightarrow \sigma_c$ and $\sigma \rightarrow \sigma_0$).

The subsequent development of the fluctuational theory of strength made it possible to get a deeper insight into the physical significance of the parameters in the Zhurkov formula. For example, it has been shown that the "zero" energy of activation must correspond to the case $\sigma \rightarrow 0$ and $T \rightarrow 0$ K. It is sometimes believed (13, 14) that the structure-sensitive parameter γ characterizes the nonuniformity of stress distribution over the chains in the polymer. At the same time it has been established (1) that the parameter γ characterizes the nonuniformity of stress distribution in the vicinity of cracks and other flaws and is the product of the dimensionless stress concentration factor and the fluctuational volume ($\gamma = \beta\omega$). The above considered version of the fluctuational theory of strength can mainly be used to describe the brittle (at $T \leq T_b$) fracture of polymers.

The basic ideas and propositions of the thermofluctuational theory have been repeatedly tested experimentally. A large series of investigations devoted to the experimental substantiation of the thermofluctuational concept of strength have been carried out by Zhurkov and his coworkers (2, 12-14, 16). In order to elucidate the fracture mechanism in polymers, they employed the methods of electron paramagnetic resonance (EPR), infrared spectroscopy and mass spectroscopy.

Subjecting polymer specimens to tensile stresses in a vacuum chamber of the mass-spectrometer, Zhurkov and his coworkers found that volatile products are really liberated; the rate of their formation increases exponentially as the stress applied is increased. This effect has also been detected in investigations of polymers with quite different chemical structures, such as polymethyl methacrylate, polystyrene, polyacrylonitrile, polypropylene, polyethylene, polyformaldehyde, polycapramide, nitrocellulose, etc. It has been found that for a number of polymers the composition of the volatiles formed during mechanical fracture is the same as during thermal degradation. But thermal degradation is a process consisting of

thermofluctuational acts. The thermofluctuational nature of the fracture process has thus been revealed by experiment.

To detect the broken chemical bonds in stressed polymer specimens, use was made of the EPR technique (2, 16). It has been found that in polymer specimens subjected to external loads the concentration of free-radicals resulting from the rupture of chemical bonds increases. A study of the kinetics of accumulation of polymeric chains ruptured under mechanical loads has shown that the rate of bond-breaking changes by an exponential law with increasing load, which is in good agreement with the variation of durability predicted by the Zhurkov formula. The chemical bonds broken during the fracture of polymers have also been detected by infrared spectroscopy. Thus, the basic premises of the thermofluctuational conception of fracture agree well with the results of investigations of the fracture process carried out by physical methods.

It should be remarked that the mechanism of the fracture of one and the same polymer may vary, depending on the test temperature range. For example, below the brittle temperature most polymers may fracture either by the athermal (Griffith) mechanism or by the thermofluctuational mechanism. Near 0 K, when thermal motion is apparently insignificant and does not affect the kinetics of the growth of microcracks, the fracture of polymers is an athermal process. At higher temperatures (but not higher than T_b), when thermal fluctuations exert a decisive effect on durability, the fracture of polymers is a thermofluctuational process. In the case of solid polymers, at temperatures $T_b < T < T_g$ both the thermofluctuational and the relaxational mechanism of fracture can occur. The latter is associated with the formation of "silver" cracks and with the development of forced-elastic strains. The phenomenon of forced elasticity, the nature of which has been elucidated by Aleksandrov (21), consists in the following: being subjected to large stresses, an amorphous polymer in the glassy state is capable of undergoing large deformations. The residual strain that develops in the polymer is retained if the polymer is in the glassy state, but it disappears if the polymer is heated to temperatures exceeding T_g . Aleksandrov (21) and Lazurkin (22) have shown that forced elasticity has a relaxational nature. The durability of polymers in the temperature range, in which forced-elastic deformation is possible, will be mainly determined by the time during which "silver" cracks spread throughout the considerable part of the specimen.

The fracture of polymers in the rubbery state (for example, elastomers) is a more complicated process governed by the viscoelastic mechanism. In this case, the durability is determined not so much by the rupture of chemical bonds as by the microviscous deformation; the result is the micro-separation of the polymer.

Bartenev and his coworkers have demonstrated that the durability of cross-linked elastomers is described well by the equation

$$\tau = B\sigma^{-m}e^{U/kT} \quad (8.27)$$

where τ is the durability; σ is the fracture stress; B and m are constants which depend on the type and structure of the polymer. It has been found that for some natural rubbers the activation energy of the fracture process coincides with the activation energy of viscous flow. This leads one to believe that the kinetics of the fracture process of elastomers is mainly governed by intermolecular bonds. The assumption of the important role of intermolecular interaction in the fracture process was first advanced by Gul (3, 23, 24), who maintains that the loading of polymers causes, in the first place, the rupture of intermolecular bonds, following which the stress on chemical bonds begins to increase.

There also exist other methods of describing the fracture of polymers, those due to Bueche (25), Gubanov and Chevychelov (18, 19), Ilyushin and Ogibalov (26).

The strength properties of polymers depend, to a considerable extent, on their chemical and physical structure. The dependence of the long-term strength on structure is specified, within the framework of thermofluctuational concepts, by the introduction of the structure-sensitive parameters γ . As a rule, the lower the value of γ , the longer the durability of the polymer. The presence of sharply prominent structural inhomogeneities leads to large stress concentrations at the flaws, thereby reducing the strength of the polymer. It is therefore clear that the formation of large spherulites in the polymer leads to a decrease in the strength. And, conversely, the fine-spherulite structure contributes to the strength.

In the case of crystalline polymers, an increase in the degree of crystallinity sometimes results in an increase in strength. This is associated with the fact that the strength of crystallites is, as a rule, higher than that of amorphous regions, which are usually the weakest sites in crystalline polymers. The chain rupture on mechanical loading occurs most often in amorphous regions. However, if the polymer has been crystallized very strongly, its strength will decrease rather than increase because of the enhanced brittleness.

The strength of polymers is most strongly influenced by the orientation. In the oriented state the forces of intermolecular interaction between neighbouring (closely spaced) extended chains add along the chain length, which leads to a substantial enhancement of intermolecular interaction. The strength of the polymer along the direction of orientation is noticeably increased. The modulus of elasticity and strength of some highly oriented polymeric fibres are equal to those of certain grades of steel (such highly oriented fibres of crystalline polymers are sometimes said to be "steel-like"). As a rule,

the strength of highly oriented polymers increases with increasing degree of crystallinity.

It seems, at first sight, that in an ideal case it is desirable to have completely crystallized fibres composed of straightened-out extended chains. Such fibres, however, will possess extremely poor deformation properties and will be very brittle. It is usually thought (27) that the following combination is optimal in a polymeric material: 50 per cent of extended chains (which would provide high values of E and σ_f) and 50 per cent of folded chains (which would provide the required deformation properties).

8.3. Effect of Relaxation Processes on Strength Properties

There exists an intimate relationship between the relaxation and strength properties of polymers. We have already said above that the fracture of some types of polymers (say, elastomers) on uniaxial extension may be treated as a viscoelastic process. Here one takes into account that the molecular processes responsible for fracture occur in a very small volume of the material. Theories describing the fracture of polymers as the growth of cracks usually take account of the fact that the molecular chains at the crack tip are stretched until they are ruptured under the action of large stress concentrations. In view of this, most of the theories of fracture used for explaining the strength of polymers point to the relationship between the viscoelastic (relaxation) and strength properties (27).

Indeed, the viscoelastic properties associated with relaxation processes taking place in polymers exert an effect on the rate of the fracture process in many cases. This happens because the rate of fracture depends on the elastic properties of polymers and on mechanical losses involved in fracture. It is natural that the mechanical losses caused by the various types of molecular motion have a strong effect on the strength of polymers. Moreover, a change in the type of molecular motion (and, hence, in the type of relaxation processes taking place in polymers) brought about by a change in temperature sometimes results in a change in the fracture mechanism and, hence, in the mode of the temperature dependence of strength. This is what exactly happens upon transition of a polymer from the glassy to the rubbery state. In the rubbery state, which involves the segmental motion of polymeric chains, the fracture process is apparently very closely connected with deformation processes and has a relaxational nature. Since the relaxation processes associated with molecular motion occur down to very low temperatures (28) (and in some polymers, down to 0 K), it evidently follows that their effect on strength properties can be detected not only in the region of the rubberlike state.

That the strength and relaxation properties of polymers are physically related to a certain extent is also seen in the following fact: the relation that takes account of the time dependence of strength (the Zhurkov formula) coincides in form with the expression for the molecular relaxation time derived and used for describing the relaxation (deformation) properties of polymers by Aleksandrov (4, 21) and Gurevich (29) before the thermofluctuational theory of strength was worked out. Indeed, while developing further the assumption made by Aleksandrov that the relaxation time τ depends not only on temperature but on the mechanical stress as well, Gurevich proposed in 1947 the following equation for the molecular relaxation time:

$$\tau = \tau_0 e^{\frac{U - \gamma\sigma}{kT}} \quad (8.28)$$

where $\tau = 10^{-12}$ s is a constant equal to the period of vibration of a kinetic unit about the temporary equilibrium position; U is the activation energy corresponding to the transition of segments from one position to another; σ is the mechanical stress (in uniaxial extension); γ is a parameter characteristic of a given polymeric material.

The intensive molecular motion, which is typical of the rubbery state, leads to the dissipation of the elastic energy from sites with a large stress concentration. This evidently accounts for the important part played by relaxation processes in the fracture of elastomers.

The close relationship between relaxation processes and strength properties is also manifested in the fact that the Williams-Landel-Ferry principle is sometimes successfully employed for describing experimental data on the strength and durability of polymers. Considering that the strength of elastomers has a viscoelastic, relaxational nature, we may presume that the use of this method is, to a certain extent, justifiable in this case.

The relationship between strength properties and molecular relaxations, which govern the entire set of viscoelastic properties of polymers, has been studied by many investigators. It has been found (30, 31) that the expression for the relative strength of viscoelastic bodies may be written as

$$\frac{R_1}{R_2} = \left(\frac{E'_1 \Delta_2}{E'_2 \Delta_1} \right)^m = \left(\frac{\rho_1 c_1^2 \Delta_2}{\rho_2 c_2^2 \Delta_1} \right)^m \quad (8.29)$$

where R_1 and R_2 are the breaking stresses; E' is the dynamic elastic modulus; Δ is the logarithmic decrement; ρ is the density; c is the velocity of sound; the subscripts 1 and 2 refer to different samples of the same polymer; the exponent m usually assumes values equal to 1 or $1/2$.

From formula (8.29) it follows that the breaking stress is proportional to the dynamic elastic modulus (the storage modulus) or to

the sound velocity squared. An analogous relation between R and E' (R and c^2) has been derived (32) through the use of the Boltzmann response equation.

A distinct correlation between strength and viscoelastic properties is revealed in investigations of oriented polymers. For example, the investigation of an oriented polyethylene terephthalate film (33) has shown that the dependence of relationship between σ_f and E' is linear and may be described by an empirical formula:

$$\sigma_f = kE' + b \quad (8.30)$$

where k and b are constants which are readily determined graphically. It appears that a clear-cut correlation between σ_f and E' is observed for samples of Lavan (polyethylene terephthalate) film having different extension ratios and produced at the same temperature. For the samples prepared at other temperatures the parameters k and b in formula (8.30) undergo change, but the character of the dependence remains the same.

It is known that relation (8.9) is arrived at in different theories of strength. The available experimental data (33) show that such a dependence [of the type (8.30) at $b = 0$] is observed not for all polymers. However, even in those cases where σ_f is proportional to E' , the proportionality factor k obtained is not equal to 0.1 (predicted by theory); it is less by about 5 times. That the factor k found experimentally is several times less than the theoretical value (0.1) can possibly be explained by the fact that the dynamic elastic modulus is inserted into formula (8.9), which usually exceeds the static modulus. On the other hand,

$$E' \approx E_0 + E_r \quad (8.31)$$

where E_0 is the static modulus of elasticity; E_r is the relaxation part of the dynamic modulus. In view of this, it becomes understandable why the straight line representing the dependence of σ_f on E' may not pass through the coordinate origin [the coefficient b in formula (8.30) is different from zero]. One factor responsible for values of the factor k in formula (8.30) being less than 0.1 is possibly the very small (as compared with theory) value of strength which is due to the specificity of the supermolecular organization or to the presence of defects in the polymer. Thus, the deviation of the ratio $\sigma_f/0.1E'$ from unity may serve, to a certain extent, as a measure of the defect content of the material (10).

There exists a definite relationship between the values of impact (dynamic) strength and relaxation processes in polymers. It has been found for a number of polymers that the impact strength below T_g is sufficiently large, if in the plot of $\tan \delta$ against temperature there is a secondary (low-temperature) peak attributable to the mobility of small kinetic units of the polymeric chain. Here it is

presumed that the temperature at which the impact strength is measured is higher than the temperature T_m of the secondary loss ($\tan \delta$) peak. If the temperature at which the impact strength is measured is lower than T_m , the effect of the secondary loss peak is found to be insignificant.

In establishing such types of correlational relationships one should take account of the time-temperature superposition principle, since the duration of the blow does not coincide with the period of acoustic vibrations.

If the intensity of the secondary peak is diminished by some reason, the impact strength may be expected to decrease. The same may be said about the impact elasticity. For example, the introduction of "antiplasticizers" into polycarbonate results in a sharp decrease in the low-temperature loss ($\tan \delta$) peak and in the impact elasticity (33). Wada attempted to establish theoretically a relationship between the impact elasticity of notched specimens and the relaxation properties of polymers. He derived the following expression:

$$I = k\gamma^2\tau^2 (G'_{100} - G')^2/G'_{100} \quad (8.32)$$

where γ is the rate of strain which is considered to be constant during the time of fracture t_0 ; τ is the relaxation time of the polymeric material, for which the Maxwell model is valid; G'_{100} is the dynamic shear modulus at $T = 100$ K; G' is the dynamic shear modulus at a given temperature; k is a constant.

Relation (8.32) has been tested experimentally for a number of polymers; it is valid provided that $t_0/r \ll 1$. It has been shown that there is a linear relationship between the impact elasticity I and

the quantity $\int_0^\infty (G''/G') dT$. This means that the impact elasticity I

is directly proportional to the area under the curve of $\tan \delta$ versus T in the temperature range from 0 to 300 K.

References

1. Bartenev, G. M. and Yu. S. Zuev, *The Strength and Fracture of Highly Elastic Materials*, Khimiya, Moscow-Leningrad, 1964 (in Russian).
2. Regel, V. R., A. I. Slutsker, and E. E. Tomashevsky, *The Kinetic Nature of the Strength of Solids*, Nauka, Moscow, 1974 (in Russian).
3. Gul, V. E., *The Structure and Strength of Polymers*, Khimiya, Moscow, 1971 (in Russian).
4. Gul, V. E. and V. N. Kuleznev, *The Structure and Mechanical Properties of Polymers*, Vysshaya Shkola, Moscow, 1966 (in Russian).
5. Askadsky, A. A., *The Deformation of Polymers*, 3rd ed., Khimiya, Moscow, 1978 (in Russian).
6. Tager, A. A., *Physical Chemistry of Polymers*, Mir Publishers, Moscow, 1972 (translated by D. S. Sobolev).
7. Born, M. and M. Goeppert-Mayer, in: *Handbuch der Physik*, Gëger-Scheel, 1933.

8. Zwicky, F., *Phys. Z.*, **24**, 6, 131 (1923).
9. Orowan, E., *Nature*, **154**, 341 (1944).
10. Kobeko, P. P., *Amorphous Substances*, Izd. Akad. Nauk SSSR, Leningrad, 1952 (in Russian).
11. Griffith, A., *Phil. Trans. Roy. Soc., A*, **221**, 587, 163 (1921).
12. Zhurkov, S. N. and B. N. Narzullaev, *Zhurn. Tekh. Fiz.*, **23**, 10, 1677 (1953).
13. Zhurkov, S. N. and S. A. Abasov, *Vysokomol. Soedin.*, **3**, 3, 441 (1961).
14. Zhurkov, S. N. and S. A. Abasov, *Vysokomol. Soedin.*, **4**, 11, 1703 (1962).
15. Aleksandrov, A. P., *Vestnik Akad. Nauk SSSR*, 7-8, 51 (1944).
16. Regel, V. R. and A. I. Slutsker, in: *Physics Today and Tomorrow*, Nauka, Leningrad, 1973 (in Russian).
17. Bartenev, G. M., *Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk*, 9, 53 (1955).
18. Gubanov, A. I. and A. D. Chevychelov, *Fiz. Tverdogo Tela*, **4**, 4, 928 (1962).
19. Gubanov, A. I. and A. D. Chevychelov, *Fiz. Tverdogo Tela*, **5**, 9, 2599 (1963).
20. Bartenev, G. M., in: *Relaxation Phenomena in Polymers*, Khimiya, Leningrad, 1972 (in Russian).
21. Aleksandrov, A. P., *Proceedings of the 1st and 2nd Conferences on High-Molecular-Mass Compounds*, Izd. Akad. Nauk, Moscow-Leningrad, 1945 (in Russian).
22. Lazurkin, Yu. S., Dissertation for Doctor's Degree, Institute for Physical Problems, USSR Academy of Sciences, 1954.
23. Gul, V. E., N. Ya. Sidneva, and B. A. Dogadkin, *Kolloid. Zhurn.*, **13**, 6, 422 (1951).
24. Gul, V. E. and I. M. Chernin, *Doklady Akad. Nauk SSSR*, **123**, 4, 713 (1958).
25. Bueche, F., *J. Appl. Phys.*, **26**, 9, 1133 (1955).
26. Ilyushin, A. A. and P. M. Ogibalov, *Mekhanika Polimerov*, **6**, 828 (1966).
27. Scott, K. W., *Polymer Eng. and Sci.*, **7**, 3, 158 (1967).
28. Perepechko, I. I., *Low-Temperature Properties of Polymers*, Mir Publishers, Moscow and Pergamon Press, Oxford, 1980 (translated by A. Beknazarov).
29. Gurevich, G. I., *Zhurn. Tekh. Fiz.*, **17**, 12, 1491 (1947).
30. Malmeister, A. K., *The Elasticity and Inelasticity of Concrete*, Izd. Akad. Nauk Latv. SSR, Riga, 1957.
31. Latishenko, V. A., *Mekhanika Polimerov*, **2**, 334 (1967).
32. Gershberg, M. V., S. V. Ilyushin, and V. I. Smirnov, *The Non-Destructive Methods of Testing of Shipbuilding Fibreglass Plastics*, Sudostroenie, Leningrad, 1971 (in Russian).
33. Perepechko, I. I., *Acoustic Methods of Investigating Polymers*, Mir Publishers, Moscow, 1975 (translated by G. Leib).

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To the Reader

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N. Voznaya

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